

Natural and Enhanced Attenuation of Soil and Ground Water at Monument Valley, Arizona, and Shiprock, New Mexico 2006 Status Report

April 2007



Office of Legacy Management



Natural and Enhanced Attenuation of Soil and Ground Water at Monument Valley, Arizona, and Shiprock, New Mexico

2006 Status Report

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Executive Summary

The U.S. Department of Energy (DOE) Office of Legacy Management (LM), the Navajo Uranium Mill Tailings Remedial Action (Navajo UMTRA) program, and the University of Arizona (UA) are exploring natural remedies for ground water contamination at DOE's Legacy Management site near Monument Valley, Arizona. DOE removed radioactive tailings from Monument Valley, a former uranium millsite, in 1994. Nitrate and ammonium, used during the milling process, remain in a shallow ground water plume spreading from a millsite source. A conventional cleanup strategy might involve drilling wells and pumping ground water to a treatment facility on the surface. Pilot studies jointly funded by LM and UA are answering two questions: What is the capacity of natural processes to remove nitrate and slow plume dispersion, and if needed, can we efficiently enhance natural attenuation? Below are highlights of findings in 2006 that bear directly on these questions.

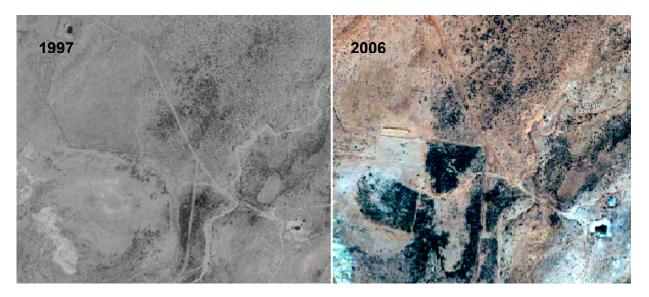
First, we have confirmed that natural microbial denitrification is occurring in the contamination plume. In 2005 we inferred that denitrification was occurring because plume nitrate samples became progressively more enriched in ¹⁵N relative to ¹⁴N with distance from the source area. In 2006, we withdrew soil samples from the aquifer and demonstrated N₂O production in laboratory microcosms incubated at 5°C and 25°C, the range of temperatures reported for plume water samples. The rate measured in microcosms was approximately the same as the rate estimated from isotope enrichment, and would support sufficient denitrification to eventually (30–50 years by rough calculations of the volume and nitrate content of the plume) remove most of the nitrate from the plume. However, denitrification activity was not uniformly distributed in the aquifer. The upper, phreatic layer where roots would be found had more denitrification activity than in deeper samples.

Second, ethanol markedly stimulated denitrification by providing a carbon substrate. Rates were 60 times higher in microcosms supplemented with ethanol than in controls. This suggests that ethanol injection into wells over the hotspot of nitrate contamination could greatly accelerate the natural remediation rate, and shorten the time needed for site cleanup. A pilot project could be conducted over the hotspot area of the plume to test the effectiveness of this enhancement.

Third, as we already suspected, moisture is a main limiting factor for denitrification activity in the the source area. Although ethanol stimulated denitrifications in the shallow soil layers, it is clear that moisture is no longer penetrating deeply into the profile. The water application rate is currently 0.16 m/year, well below the evapotranspiration (ET) capacity of the plants. The irrigation rates could be increased to at least double that value. This is technically feasible with the existing irrigation system, by operating it for longer each day. Ethanol could also be injected into the irrigation lines as a further enhancement of denitrification.

Fourth, excluding grazing has a major effect on plant density and ET. After just a single growing season since exclosure plots were constructed to prevent grazing by livestock, ET was twice as high in the exclosure plots than in the grazed area surrounding the exclosures. Mean ET rates projected over the exclosure plot were 5 mm/day, or about 0.5 m/yr. This rate exceeds annual precipitation and could be a method for controlling recharge over the plume and for withdrawing water from the plume.

The longer term effect of controlling grazing is seen in the figure below, comparing the site in 1997 with 2006. The northeast corner of the fenced area (dark area near the center of the 2006 photo) has developed a thick growth of phreatophytes, with 69% plant cover. Very little grew in that area in 1997. Hence, controlling grazing over at least part of the plume (the hotspot ares) could markedly enhance natural remediation by 1) controlling the movement of water downgradient from the hotspot and 2) supplying a carbon source for denitrification in the phreatic zone of the hotspot. An enhanced plant community over the hotspot area would also increase the rates of nitrogen and sulfur uptake by plants over the plume.



Comparison of vegetation in the fenced source area (lower left quarter) in 1997 and 2006.

1.0 Introduction

The U.S. Department of Energy (DOE) is conducting pilot studies of enhanced attenuation remedies for contaminated ground water at former uranium mill tailings sites near Monument Valley, Arizona, and Shiprock, New Mexico. At Monument Valley, nitrate, ammonium, and sulfate levels are elevated in an alluvial aquifer spreading away from a source area where tailings have been removed. At Shiprock, nitrate, sulfate, and uranium concentrations are elevated in ground water near a disposal cell constructed to contain uranium mill tailings in place.

A DOE environmental assessment mandated pilot studies at Monument Valley to evaluate and demonstrate alternative remedies before a final strategy is selected (DOE 2004a). Preliminary studies suggested that natural and enhanced phytoremediation may be viable options for reducing nitrate and sulfate levels in the alluvial aquifer and at the plume source, and are consistent with revegetation and land management goals for the site (DOE 2002, 2004b). Phytoremediation relies on the roots of plants to remove, degrade, and slow migration of contaminants.

In May 2005, DOE and the Navajo Nation jointly approved a second and final phase of pilot studies as proposed in a work plan published by DOE in 2004 (DOE 2004c). The purpose of the final phase is to evaluate the capacity of natural processes and methods to enhance natural processes that degrade and slow migration of contaminants both in the alluvial aquifer and at its source. The pilot studies are focusing on phytoremediation and microbial denitrification processes. In 2006 DOE published first-year (2005) results and a strategy for using results to select a final remedy (DOE 2006). Section 2.0 of this report is a brief review of the enhanced attenuation approach. Summaries of second-year (2006) results of the Monument Valley pilot studies are presented in Section 3.0 of this report.

Phytoremediation studies commenced in 2006 at the Shiprock site to evaluate the use of plants to remove ground water through uptake and transpiration as a way to contain or hydraulically control the migration of ground water contaminants. Summaries of the 2006 phytoremediation tasks at Shiprock are presented in Section 4.0 of this report.

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2.0 Natural and Enhanced Attenuation Strategies

Conventional remedies for contaminated soil and ground water focus on engineered systems such as excavating and hauling large volumes of soil to engineered landfills, and drilling wells to pump large volumes of ground water to the surface for treatment. In contrast, reliance on natural processes to clean up contamination, referred to as Monitored Natural Attenuation (MNA), has increased in response to greater awareness of the limitations of engineered remedies for achieving ground water and soil remediation goals (EPA 1999, NRC 2000). However, the capacity of natural processes alone may not be adequate to attain remediation goals in a timely manner. At sites with uranium mill tailings contamination, natural attenuation can be used to manage ground water contamination remaining after engineering approaches have removed or isolated the source of contamination (DOE 1996).

Enhanced Attenuation (EA) is a strategy that bridges the gap between active, engineered solutions, and passive MNA (SRNL 2007). EA involves human intervention to enhance or accelerate natural processes. Successful enhancements should increase the magnitude of natural attenuation processes beyond what would occur without intervention (SRNL 2006). A successful enhancement is also a sustainable manipulation—it does not require continuous, long-term intervention. In many cases, sustainable enhancements of natural processes are needed to achieve a favorable mass balance between the release of contaminants from a source (contaminant loading) and processes that degrade or retard migration of contaminants down gradient in the plume.

These pilot studies are designed to evaluate MNA and EA as the primary components of a final remedy for the alluvial aquifer at the Monument Valley site (DOE 2004b). Figure 2–1 illustrates a decision framework for using the pilot study results to choose a final strategy. The framework is based on the assumption that natural and sustainable processes existing at the site have the capacity, either with or without enhancements, to remediate source area soils and the alluvial aquifer in an acceptable time frame. An overview of the steps of the decision process was provided in the 2005 status report (DOE 2004c, Section 4.0).

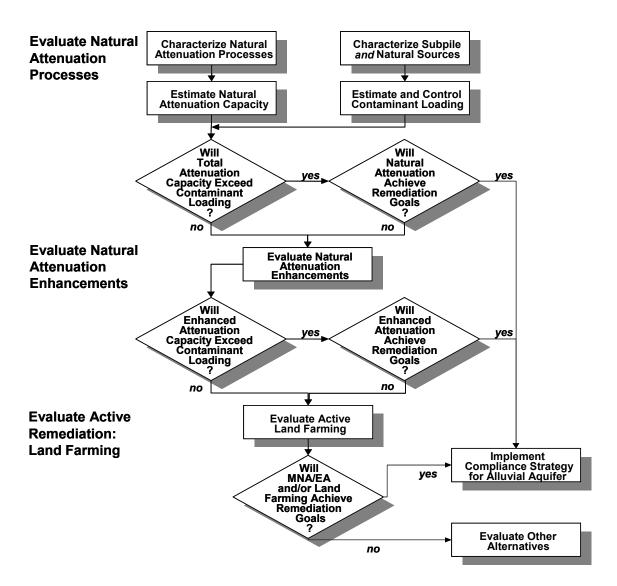


Figure 2–1. Framework for applying pilot study results to choose a final remedy for the alluvial aquifer at Monument Valley.

3.0 Monument Valley Pilot Studies

Monument Valley pilot studies are answering two questions: What are the capacities of natural attenuation processes to remove nitrate and slow plume dispersion, and can we efficiently enhance natural attenuation? The pilot studies are evaluating natural and enhanced attenuation of both the nitrate plume and its source. Details of the rationale for and descriptions of all Monument Valley pilot study tasks are available elsewhere (DOE 2004c, DOE 2006). Only summaries of tasks conducted during Calendar Year 2006 are presented in this section.

3.1 Source Containment and Removal

In 1994, DOE completed a mandated remediation of *radioactive* constituents in tailings and soils at the site. Materials with radium-226 concentrations exceeding 15 picocuries per gram were removed and hauled to a disposal cell near Mexican Hat, Utah. However, in 1997, sampling within the footprint of a former tailings pile (subpile soil) revealed elevated levels of ammonium and nitrate, ranging from 45–1,060 mg kg⁻¹ and 0–273 mg kg⁻¹, respectively. The subpile soil is assumed to be a continuing source of contamination for the alluvial aquifer extending to the north.

This section provides summaries of work conducted in 2006 on the following tasks. Task numbers are from the 2004 work plan (DOE 2004c).

- Determine Causes and Recourses for Stunted Plant Growth (Task 5.4.3)
- Monitor Soil Water and Recharge (Task 5.4.5)
- Monitor *Atriplex* Canopy Growth and Total N (Task 5.4.6)
- Enhance Microbial Denitrification in the Source Area. This is a follow-up activity of Evaluate Natural Denitrification Processes (Task 5.4.7)

3.1.1 Causes and Recourses for Stunted Plant Growth

An area of poorer plant growth occurs in the western third of the 1999 subpile soil planting. Previous analyses of soil samples from areas with both poor and good growth suggested that nitrate, sulfate, calcium, magnesium, strontium, and vanadium were higher in the poor-growth area. Conversely, concentrations of iron, manganese, phosphate, potassium, sodium, and uranium concentrations were significantly lower in the poor-growth area. The stunted growth of *Atriplex* shrubs may be due to the combined effects of both an excess and a deficiency of several ions. In a previous greenhouse study, growth of Sudan grass in soil obtained from the poor-growth area was significantly less than growth in a soil sample taken from a good-growth area. Chemical analysis of Sudan grass tissue samples was inconclusive as to the causative agent(s) of poor growth. Tests also found that soil bulk densities, another suspected cause of poor plant growth, were not significantly different in poor-growth and good-growth areas.

Greenhouse and field studies were conducted in 2006 to identify recourses for poor *Atriplex* growth.

3.1.1.1 Greenhouse Study

Diné College in Tsaile, Arizona, was funded to conduct a greenhouse study to evaluate amendments that either supply plants with adequate micronutrients or suppress phytotoxic effects. The study consisted of 4 soils, 10 fertilizer solutions, and 1 plant species:

Soils

Poor Growth (stained) Soil

Good Growth Soil (collected out side of the stained area),

Mixture of 2 parts Stained soil to 1 part Miracle-Gro All-purpose Potting Mix

Mixture of 2 parts Good Growth Soil to 1 part Miracle-Gro All-purpose Potting Mix

Fertilizer Solutions

Water Only

Iron: 10, 20 and 40 parts per million (ppm) iron chelate

Copper: 10, 20 and 40 ppm cupric chloride

Iron and Copper Mixture: 10, 20 and 40 ppm iron chelate and cupric chloride

Plant Species

Fourwing saltbush (Atriplex canescens)

Table 3–1 list the components of the study and will be useful when comparing the plants photographed in Figure 3–1 and Figure 3–2.

Table 3–1. Percent survival for soil and fertilizer treatment combinations (n=4 plant replicates per treatment) for a total of 88 plants.

Treatment	Soil	Fertilizer	% Survival
Α	Stained MV	Negative Control	50
В	Stained MV	Low Fe	100
С	Stained MV	Med Fe	50
D	Stained MV	Hi Fe	25
E	Stained MV	Low Cu	25
F	Stained MV	Med Cu	75
G	Stained MV	Hi Cu	50
Н	Stained MV	Low Fe + Cu	25
I	Stained MV	Med Fe + Cu	50
J	Stained MV	Hi Fe + Cu	0
K	Stained MV + MG	Slow-release fertilizer	0
L	Stained MV + MG	Low Fe	25
М	Stained MV + MG	Med Fe	50
N	Stained MV + MG	Hi Fe	50
0	Stained MV + MG	Low Cu	75
Р	Stained MV + MG	Med Cu	75
Q	Stained MV + MG	Hi Cu	50
R	Stained MV + MG	Low Fe + Cu	100
S	Stained MV + MG	Med Fe + Cu	100
T	Stained MV + MG	Hi Fe + Cu	75
U	Good MV	Field (Good/Positive)	0
V	Good MV + MG	Positive w/fertilizer	100



Figure 3–1. Composite photograph of the Atriplex plants for treatments A (a and b) and K (c and d) at the start of the experiment (May 15, 2006; a and c) and 2 months later (July 6, 2006; b and d) showing the senescence of leaves over the course of the study.



Figure 3–2. Composite photograph of corn plants sown in un-supplemented soil (Treatments A through J) and soils supplemented with potting mix (Treatments K through T).

Plants were transplanted into 1.0-liter (L) pots and cut to an initial height of 17 centimeters (cm) above the rim of the pot. Initial biomass measurements were obtained when plants were potted. Plants were irrigated (0.5-1.0 L) every other day according to the treatment schedule listed in Table 3–1. Plant height and width measurements were taken weekly as well as plant mortality. After 60 days of growth a final biomass measurement was taken to calculate the average relative growth rate (RGR) as:

$$\%RGR = \frac{\ln(biomass_{final} - biomass_{initial})}{\# days} * 100$$

Atriplex plants did not respond well to any treatment and the overall plant survival rate after 60 days of growth was 53%. All plants lost, instead of gained, biomass as shown in Figure 3–1 making it difficult to draw any conclusions from this dataset. The cause of poor growth may have been transplant shock.

As a way of satisfying our objective of providing educational opportunities for Diné College students, the study was repeated in exact detail but with corn (*Zea mays*), a plant that can be grown from seed. Early results of the corn study were documented by photography and looked promising as shown in Figure 3–2. For example, plant growth in the stained soil with potting mix (treatments K through T) was far superior to plant growth in the stained soil without potting mix (treatments A through J) regardless of fertilizer treatment.

Unfortunately, this study was prematurely ended when a cow gained access to the greenhouse and consumed all the plant material before any biomass measurements could be taken.

3.1.1.2 Field Study

A nutrient study was installed in the source area planting in April 2006 to supplement the greenhouse study. A mulch was mixed into the soil of designated transplants in the poor-growth (stained) soil area as a way to improve growth. Selected plants were tagged appropriately (Figure 3–3). Miracle-Gro potting mix was placed in a small hole and *Atriplex* were placed in the mulch, not in the soil. *Atriplex* designated for no mulch were planted in similar size holes except the displaced native soil was replaced while transplanting. The study consisted of 4 treatments, 8 plants/treatment, for a total of 32 plants:

No Fertilizer

Fertilizer Only (2L of 40 ppm Fe + Cu)

Mulch Only (Miracle-Gro Potting Mix)

Fertilizer + Mulch

Each month, from April through September 2006, each of the 16 plants designated for fertilizer with 2L of 40 ppm Fe + Cu were irrigated with 12.92 g SEQUESTAR® 6% IRON CHELATE and 2.05 g CuCl₂ - dihydrate mixed into 5 gallons of water.

At the end of the growing season (October 2006) plant height and width were measured and converted into plant volume values for all 32 plants in the study. Average plant canopy cover for treated and untreated plants were compared. Results are presented in Table 3–2 along with Fisher's Least-Significant-Difference Test matrix of probabilities resulting from comparing the means (Table 3–3) between cases listed in Table 3–2.

Analysis of Variance (ANOVA) show that of the 2006 plantings in poor-growth soils, untreated plants are not growing as well as plants treated with mulch + fertilizer (p = 0.025) or plants treated with fertilizer alone (p = 0.048). Plants treated with just mulch performed only slightly yet not significantly better than the untreated plantings. Furthermore, the eight plants left untreated within the poor growth rows appeared to have the lowest average plant canopy cover compared to the other three treatments, but the values were not significantly different at the 95% confidence level. These results suggest that it is possible to enhance plant growth in the stained (poor-growth) portion of the subpile planting using mulch and fertilizer applications.

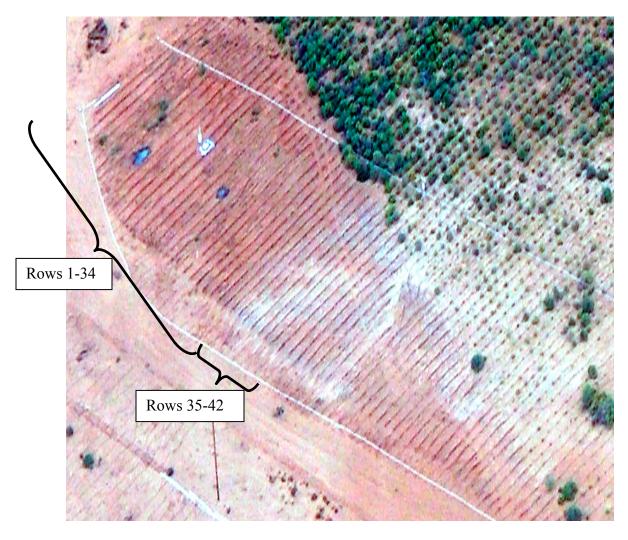


Figure 3–3. Ariel photograph of the Extended Field North showing planting rows. Plants in the poorgrowth (stained) soil occur in rows 35–42; plants in the control soil were in rows 1–34.

Table 3–2. Plant canopy area ($cm^2 \pm SEM$) for fertilizer/mulch treatments in study of recourses for poor plant growth in the "stained" area of the 2006 subpile planting.

Case Number	Treatment	Row Numbers	Number of Samples	Average plant canopy (cm²)			
Case A	None	1-34	34	508 (±98)			
Case B	None	35-42	8	831 (±276)			
Case C	Mulch + Fertilizer	35-42	8	1,300 (±334)			
Case D	Mulch only	35-42	8	1,125 (±531)			
Case E	Fertilizer only	35-42	8	1,203 (±424)			
ANOVA F-test = 2.288							
ANOVA P-value = $0.070 \ (\alpha = 0.05)$							

Table 3–3. Matrix of paired probabilities for the five cases listed in Table 3–2 as determined using the Fisher's Least-Significant-Difference Test.

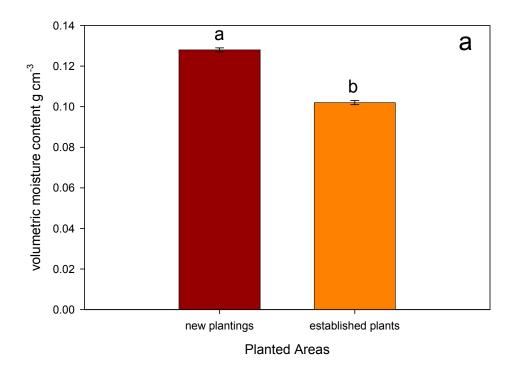
Case	Α	В	С	D	E
Α	1.000				
В	0.352	1.000			
С	0.025	0.290	1.000		
D	0.078	0.506	0.692	1.000	
Е	0.048	0.400	0.826	0.860	1.000

3.1.2 Soil Water and Recharge Monitoring

The original subpile (source area) phytoremediation plot has been irrigated each year since it was installed in 2000, with the exception of 2003. The plants are purposely under-irrigated to prevent leaching of nitrate from the subpile into the aquifer. Irrigation volumes have ranged from 0.16 meter per year (m/yr) to 0.36 m/yr during years with irrigation, with water provided daily through drip emitters from March to October. Initially soil moisture levels were measured monthly at 0.3 m intervals to 5 m depths at 20 neutron hydroprobe stations arrayed within the established field to track wetting fronts and soil moisture profiles. In 2005, 40 new probe ports were installed in the expanded subpile phytoremediation area and in the evaporation pond area (see DOE 2006, Section 3.5). In 2006, 4 water flux meters and 16 water content reflectometers were installed for continuous monitoring of percolation flux and soil moisture profiles.

3.1.2.1 Neutron Hydroprobe Monitoring

Volumetric soil moisture was monitored using a neutron thermalization hydroprobe for all hydroprobe ports located within the source area. As in previous years, readings were taken at 0.3 m increments to the bottom of the ports (about 5.0 m except where bedrock or ground water occur at shallower depths). Volumetric water content was averaged across depth and time for the all established (1999) and new (2006) plantings (Figure 3–4a) as well as for each zone separately (Figure 3–4b) in the source area.



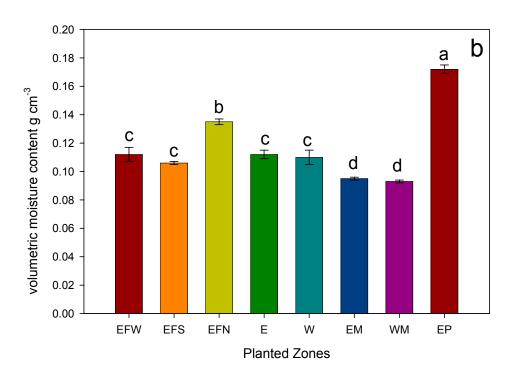


Figure 3–4. Volumetric soil moisture content averaged across depth and time for all zones within the established and new planting areas (a) and for individual zones (b). Error bars represent standard error of the mean and different letters over bars represent significant differences at alpha = 0.05.

In addition, the distribution of soil moisture over the site was plotted as a function of soil depth for each zone (Figure 3–5).

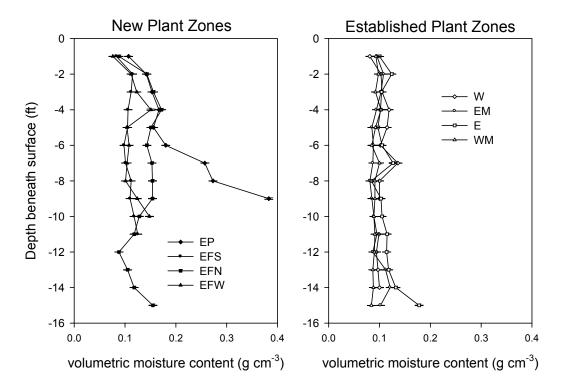


Figure 3–5. Volumetric soil moisture content with depth averaged over time for all zones within the new planting and the established plant zones (b). Error bars represent standard error of the mean and different letters over bars represent significant differences at alpha = 0.05.

On the average, the soil profile for the established field was significantly drier than the soil profile for the new plantings (p < 0.05; Figure 3–4a). This was especially evident between the 1-2 m depth (Figure 3–5), probably where roots are most concentrated. The Evaporation Pond soil was significantly (p < 0.05) more moist across depths (Figure 3–4b) and with depth (Figure 3–5, new plantings). A shallow alluvial aquifer already existed in this area even before it was planted and irrigated and the soil is saturated (volumetric water content > 0.3) at and below 9 feet (ft) for all ports (data not shown). The East Middle and West Middle zones of the established field were similar yet significantly drier (p < 0.05) than the other two zones in the established field (West and East) as well as all the new planting zones. No differences were found between the overall moisture content of the soil profile in W and E zones of the established field and the Extended Field West and Extended Field South (EFS) zones of the new plantings. Of the new planting zones, the Extended Field North was the wettest (p < 0.05) zone.

3.1.2.2 Water Content and Flux Monitoring

Water Content Reflectometers (WCRs) and Water Flux Meters (WFMs) were installed at four locations within the subpile plantings for real-time monitoring of soil moisture profiles and percolation flux. Monitoring is necessary to confirm that irrigation water is not moving below the root zone and potentially leaching contaminants. Instrument clusters were installed in the south central area of the 1999 planting (WFM1), and in the northeast (WFM2), northwest

(WFM3), and southeast (WFM4) areas of the 2006 planting. Instrument clusters consisted of one WFM placed about 370 cm deep in the soil profile with four WCRs placed above the WFM at 30-60, 90-120, 180-210, and 270-300 cm depths.

WCRs, manufactured by Campbell Scientific (www.campbellsci.com), consist of two parallel rods attached to an electronic signal generator. A pulsed wavelength traveling down a coax or waveguide is influenced by the type of material surrounding the conductors. If the dielectric constant of the material is high, the signal propagates slower. Because the dielectric constant of water is much higher than most other materials, a signal within a wet or moist medium propagates slower than in the same medium when dry. The reflectometer measures the effective dielectric as a pulse transit time, which in turn is calibrated against water content.

WCRs were calibrated at the Environmental Sciences Laboratory following the methods of Kim and Benson (2002). The procedure involves (1) compacting a soil to a specified dry bulk density for 3 different moisture contents ranging from wetter than air-dry moisture content to slightly above the optimum moisture content as, specified by the Standard Proctor Test, and (2) inserting a WCR into the soil to obtain a reading. The procedure was repeated 3 times. A linear calibration was used, so the products of the calibration were coefficients of a linear regression of the three sets of data.

The WFMs installed near the bottom of the root zone and are capable of directly monitoring saturated and unsaturated water fluxes ranging from 0.02 millimeter per year (mm/yr) to more than 1,000 mm/yr (Gee et al. 2002). The WMFs, developed by Pacific Northwest National Laboratory, feature a funnel to direct water from the soil into a passive wick for moisture tension control, a miniature tipping bucket for real-time flux measurements that can be calibrated from the surface, and a pipe or chimney extending above the funnel to minimize divergent flow. Two WFMs were installed in March 2006; the other two were installed in July 2006.

A summary of installation steps for WFMs at Monument Valley follows:

- 1. A 4-m-deep, 15-cm-diameter test hole was hand augered at each WFM location. Excavated soils were stored in 3.8-L buckets to maintain field moisture contents. A volume sampler was used to acquire soil samples every 30-60 cm to determine soil dry-weight bulk density and moisture content. These data were used to calculate lift mass, which was needed to reconstruct the soil profile above the WFM to match the original compaction.
- The 15-cm-diameter holes were reamed with a 30-cm-diameter hand auger to a depth of about 4 m. Again, excavated soil was stored in 3.8-L buckets to maintain field moisture contents.
- The tipping calibrations (volume of water per tip) in the WFMs and the calibration and sample collection tubes were checked, placed, and the hole was backfilled. The WFM funnel was initially filled to a depth of at least 2 cm with diatomaceous earth to prevent soil from filtering down through the funnel and to create good contact with wick fibers. Soil was then placed in the funnel above the diatomaceous earth, in lifts that matched the initial bulk density.
- 4. After the divergence column on the top of the WFM and the hole above the WFM were backfilled, a falling-head technique was used to determine field K_{sat} following the methods of Bagarello et al. (2004). Paired K_{sat} tests were conducted, one overlying the reconstructed

- soil profile above the WFM and the other adjacent to it on undisturbed soil. The purpose was to measure the effects of the WFM installation on the hydraulic properties of the CSL.
- 5. Four WCRs (Campbell Scientific model CS625) were installed in the reconstructed soil profile above each WFM at the depths indicated above. WCRs were placed with rods extending vertically. WCR cables were routed through PVC conduit extending above the soil surface to protect cables from rodents.
- 6. A pre-programmed datalogger (Campbell Scientific model CR205) was installed on a tripod, and WFMs and WCRs were wired to the datalogger. The CR205s communicate with a single CR1000 datalogger where data is transmitted to Grand Junction via a cell phone modem.

The four WFMs have recorded zero percolation since they were installed in March and July 2006. These results support the conclusion that infiltration from the combination of ambient precipitation and irrigation has been stored on the fine sand profile and is not percolating and leaching nitrate. In December 2006, water was injected in the WFM calibration tubes and all instruments recorded tips showing that all were functioning correctly and capable of recording percolation events should they occur.

Results from WCRs placed above WFMs (Figure 3–6) show that soil water content (volumetric) is somewhat variable both spatially and temporally. The highest volumetric water content values (~16%) occurred at the 180–210-cm depth in the mature 1999 planting (WFM1), while the lowest values (~2%) occurred a the 270–300-cm depth in the southeast area of the 2006 planting (WFM4), the opposite of what would be expected if irrigation rates were uniform across the plantings. However, the greatest seasonal change in water content did occur in the more mature 1999 planting, as would be expected. By late fall 2006, water content at all depths at all four locations (except for the 270–300-cm depth at WFM2) was decreasing indicating that soil profiles were drying in response to evapotranspiration and the end of seasonal irrigation. As of January 2007, water content was still on the rise and approaching field capacity (estimated at about 13%) deep in the profile at WFM2. Roots of the first-year *Atriplex* at WFM2 were likely too shallow to draw water from the 300-cm depth.

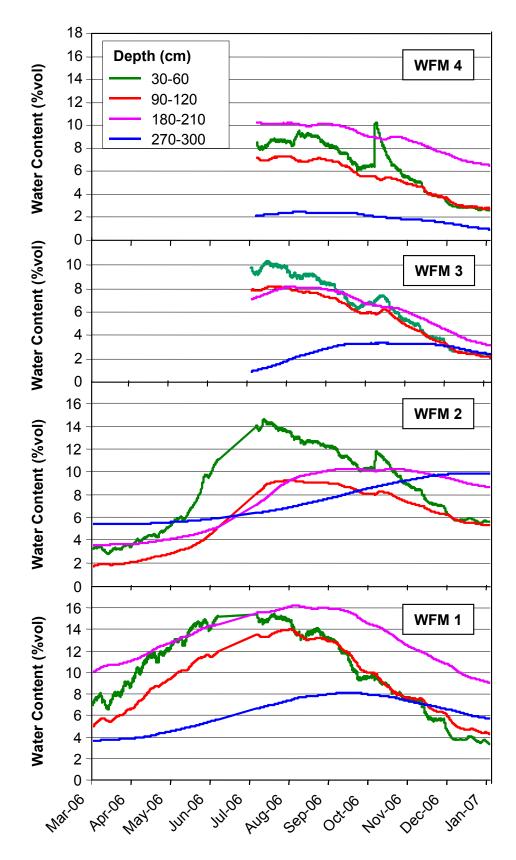


Figure 3–6. Hourly volumetric water content at four depths down to 300 cm monitored at WFM Stations WFM1, WFM2, WFM3, and WFM4.

3.1.3 Canopy Growth and Total Nitrogen

About 1.7 hectares (ha) of the subpile source area was planted in 1999, mainly with the native desert shrub, *Atriplex canescens* (fourwing saltbush), to function as a phytoremediation cover. The purposes were (1) to create a water balance cover, limiting deep percolation and seepage of nitrate, and (2) to extract nitrate converting it into plant tissue. The rectangular irrigated plot was planted with approximately 4,000 *Atriplex* seedlings grown from seed collected on Navajo Nation land and raised in a greenhouse at the University of Arizona. In March 2006, the remaining 1.6 ha of the source area (subpile soil and evaporation pond soil) was planted and irrigated. A total of 3.3 ha of the source has now been planted with a phytoremediation cover and over 7300 plants are now growing in the irrigated planting. *Atriplex* shrub growth and nitrogen uptake have been monitored since 2000.

In October 2006, the height and width of every tenth plant in each irrigated row was measured in both the 1999 and 2006 plantings. Plant biomass was estimated using a regression with plant canopy volume, a double sampling relationship established previously. Subsamples of leaves and stems from ten plants were analyzed to estimate plant nitrogen content.

Table 3–4 presents plant survival and growth results for 2006. Survival was greater than 90% for all plots. In the 1999 plots, plant cover ranged from 29% in areas where growth has been stunted (see Section 3.1.1) to over 68% in areas of best growth, with a mean plant cover of 47%. Although canopy cover for *Atriplex* planted in 2006 was low, plants grew substantially over the season.

Table 3–4. Survi	val and plant cove	er by ground	l measurements.
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Area #	Area name	Total Area (m²)ª	Plant Cover (%)	Plant Cover (m²)	Live Plants	Survival (%)
Area 1a	4 Acre Field West	3,729	28.74	1,163.25	555	90.24
Area 1b	4 Acre Field West Middle	4,807	36.74	1,486.95	872	96.35
Area 1c	4 Acre Field East Middle	4,541	51.77	2,095.22	964	96.40
Area 1d	4 Acre Field East	4,255	68.23	2,761.12	953	93.78
Area 2	Extend field west	3,016	0.84	24.90	774	91.60
Area 3	Extend field north	4,374	2.63	111.82	1,317	96.34
Area 4	Extend field south	5,427	0.71	38.06	1,240	93.87
Area 6	Evaporation pond	2,859	0.34	9.66	634	95.77
Total		33,008			7,309	

^aby QuickBird

Table 3–5 is a summary of canopy volume, dry-weight biomass, and plant tissue nitrogen results. Mean nitrogen content of the established plants was 2.17% and the new plantings contained 1.60% nitrogen. Total nitrogen uptake from 2000–2006 was 192 kg. The mean standing biomass in the 1999 planting is now 5.2 t/ha.

Table 3–5. Measured and estimated canopy volume and dry-weight biomass.

Area #	Area Name	Canopy Volume (m³)	Dry Biomass (kg)	Dry Biomass (kg/ha)	Nitrogen Uptake (kg)	Nitrogen Uptake (kg/ha)
Area 1a	4 Acre Field West	945.06	1,376.60	3,692	29	80
Area 1b	4 Acre Field West Middle	1,204.79	1,589.13	3,306	34	72
Area 1c	4 Acre Field East Middle	1,682.08	2,210.35	4,867	48	107
Area 1d	4 Acre Field East	2,751.24	3,593.67	8,847	78	192
Area 2	Extend field west	5.50	32.58	109	0.5	1.7
Area 3	Extend field north	27.74	79.26	181	1.2	2.9
Area 4	Extend field south	8.15	51.35	94	0.8	1.5
Area 6	Evaporation pond	1.15	22.31	78	0.4	1.2
			8,955		192	

3.1.4 Enhanced Microbial Denitrification in the Source Area

Planting and irrigating the source area has been exceptionally effective in removing nitrate from the soil by the microbial process know as denitrification, the conversion of nitrate to nitrogen gas. Nitrification is the conversion or oxidation of ammonium to nitrate, which can be brought about by nitrifying bacteria. The 2000–2005 results showed that loss of nitrate (denitrification) was greatest at times of peak soil moisture. In 2005, the initial rapid rate of denitrification subsided due to a decrease in soil moisture, likely caused by greater transpiration from the maturing plant community. Denitrification rates in the Monument Valley soil are also likely to be limited by low levels of total organic carbon. Previous batch studies showed that ethanol greatly enhances denitrification, hence, the possibility of stimulating denitrification by supplying ethanol through the irrigation system was evaluated.

A pilot study conducted in 2006 evaluated the addition of ethanol as a carbon source to enhance or speed up denitrification in the source area. Ethanol was distributed through a few of the subpile irrigation lines using venturi injection systems. A 15% ethanol solution was injected into drip lines to deliver a final ethanol concentration of 0.15%. The ethanol solution was replenished every month from May until September 2006. Three venturi systems were installed starting on the southeast end of the 1999 planting and distributed through irrigation tubing into the EFS, a 2006 planting. Three lines were set in place such that they fed ethanol to three irrigation lines in the 2006 planting (five plants per line) and three irrigation lines (five plants per line) in the new planting area. Three control lines in 1999 and 2006 areas directly adjacent to the venture fed lines were monitored for comparison. For plants that were irrigated with off the temporary venturi systems irrigation from the original drip system was plugged.

Soil samples were collected in May, June, July, and September 2006 to monitor for nitrate, ammonia, nitrous oxide production, and moisture at 3 ft depth (0.3, 1.3, and 2.7 m) for a total of 36 samples per sampling event. Denitrification was measured in laboratory microcosms in soil samples collected near randomly selected plants in each treatment. Denitrification was assayed by the production of nitrous oxide in incubation vessels containing acetylene, which blocks the conversion of nitrous oxide to dinitrogen gas.

Nitrous oxide production rates varied considerably from month to month (Figure 3–7) regardless of treatment with ethanol. July had the highest levels across all treatments (p = 0.043). Overall, ethanol was found to a have a significant, stimulatory effect on denitrification (p = 0.047) and rates were higher for the 0.3 m depth (p = 0.042) especially for the established plantings (p = 0.001). (See Table 3–6 for the ANOVA p-values and interaction terms).

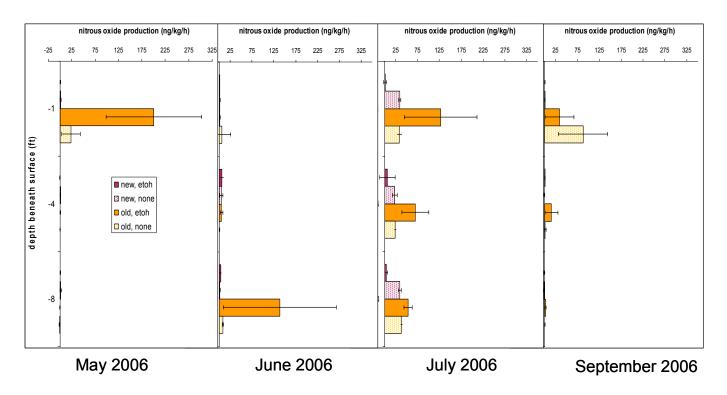


Figure 3–7. Nitrous oxide production at depth for the four sampling events. Error bars represent the standard error of the mean.

In general and despite daily irrigation, the gravimetric water content of the soil (Figure 3–8) was less than 0.1 (g/g) and was significantly drier for the established plants (p < 0.001) and with depth (p < 0.001). In September the soil was drying in the more mature 1999 planting but getting wetter with depth in the new 2006 plantings.

As a way of investigating the limiting factors for soil denitrification, a multiple linear regression analysis (Table 3–7) was conducted comparing nitrous oxide production rates with moisture, soil nitrate-N concentrations, soil ammonium-N, and TOC (taken only for May and September). Nitrous oxide production (denitrification) was most influenced by soil moisture content (r = 0.429, p < 0.05) (Table 3–8) at alpha = 0.05).

Table 3–6. Analysis of Variance with N_2 O-N (ng/kg/h) as the dependent variable and the following categorical values: plantings (2 levels, 1999 planting and 2006 planting), depth (3 levels, 1, 4, & 8 ft), date (4 levels, 5/18/2006, 6/8/2006, 7/13/2006, 9/17/2002 and the effect of ethanol (2 levels, with or without). N: 144, Multiple R: 0.701, Squared Multiple R: 0.491

Source	Sum-of- Squares	df	Mean-Square	F-ratio	Р
Planting (old versus new)	29,424.706	1	29,424.706	11.645	0.001
DEPTH (1, 4 & 8 Ft)	16,586.844	2	8,293.422	3.282	0.042
ETOH (with or without)	10,269.333	1	10,269.333	4.064	0.047
Date (May, June, July & Sept)	21,323.792	3	7,107.931	2.813	0.043
Plantings*Depth	14,605.400	2	7,302.700	2.890	0.060
Plantings* ETOH	12,464.308	1	12,464.308	4.933	0.029
Plantings*Date	1,000.177	3	333.392	0.132	0.941
Depth*ETOH	2,034.842	2	1,017.421	0.403	0.670
Depth*Date	28,080.939	6	4,680.157	1.852	0.097
ETOH*Date	6,650.162	3	2,216.721	0.877	0.456
Plantings*Depth*ETOH	2,079.189	2	1,039.595	0.411	0.664
Plantings*Depth*Date	28,895.590	6	4,815.932	1.906	0.088
Plantings*ETOH*Date	7,947.915	3	2,649.305	1.048	0.375
Depth*ETOH*Date	26,894.453	6	4,482.409	1.774	0.113
Plantings*Depth*ETOH*Date	26,125.043	6	4,354.174	1.723	0.124
Error	242,583.211	96	2,526.908		

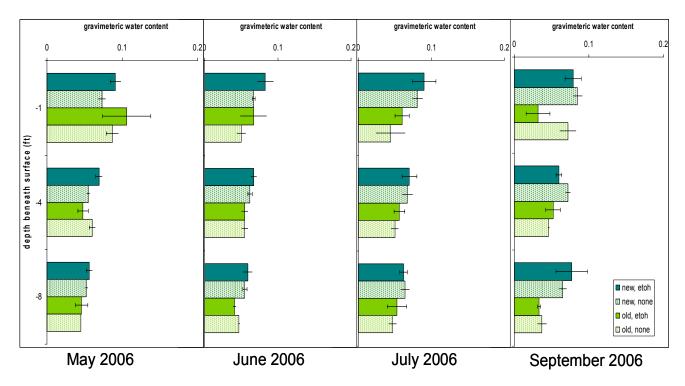


Figure 3–8. The soil gravimetric water content with depth for the four sampling events. Error bars represent the standard error of the mean.

Table 3–7. Pearson correlation matrix for all variables analyzed in the ethanol supplemented field study

	Moisture	N ₂ O-N	NH₄-N	NO₃N	TOC
Moisture	1.000				
N ₂ O-N	0.436	1.000			
NH ₄ -N	0.102	-0.069	1.000		
NO ₃ N	-0.031	-0.148	-0.031	1.000	
TOC	0.132	0.093	-0.256	-0.092	1.000

Table 3–8. Regression analysis with N_2 O-N (ng/kg/h) as the dependent variable and moisture, ammonium-N, nitrate-N and TOC as independent variables. N: 72, Multiple R: 0.471, Squared Multiple R: 0.222

Effect	Coefficient	Std Error	Std Coef	Tolerance	t	P(2 Tail)
Constant	-39.818	19.938	0.000	•	-1.997	0.050
Moisture	1,048.070	258.537	0.445	0.963	4.054	0.000
NH ₄ -N	-0.625	0.584	-0.121	0.913	-1.071	0.288
NO ₃ N	-0.244	0.192	-0.138	0.988	-1.275	0.207
TOC	-2.533	32.345	-0.009	0.900	-0.078	0.938

TOC measurements, taken at the beginning and end of the field study, are presented in Table 3–9. TOC measurements doubled for all soil samples regardless of treatment suggesting a significant amount of lateral flow and mixing from the irrigation. This may explain why very few differences were observed between treatments but does not explain why rates of denitrification were lower in September than in July.

Table 3–9. Soil TOC levels for 1, 4, and 8 ft for ETOH treated and untreated soil before (May 2006) and after (September 2006) the field study. Values in parenthesis are the standard error of the mean.

	Untrea	ated Soil	ETOH treated soil		
Depth beneath surface	May 2006	September 2006	May 2006	September 2006	
1 ft	0.215 (0.05)	0.567 (0.06)	0.193 (0.07)	0.525 (0.06)	
4 ft	0.155 (0.04)	0.467 (0.02)	0.170 (0.04)	0.417 (0.03)	
8 ft	0.128 (0.04)	0.417 (0.04)	0.108 (0.04)	0.450 (0.08)	

A microcosm study was conducted in June 2006 using composite samples of soils collected at depth near plants that had been irrigated with ethanol (ETOH treated soil) for 1 month, and at depth near plants growing in untreated soil. For the microcosm study, the moisture content of the composite soils was raised to saturation (c.a. 20% gravimetric water content) with water that either did or did not contain ethanol (0.2%, ETOH). Nitrous oxide production (denitrification) was significantly greater ($p \le 0.002$) in microcosms with than without ethanol (Figure 3–9), in contrast with the field results.

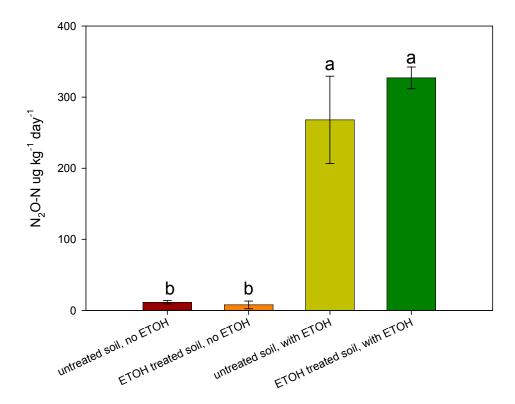


Figure 3–9. Nitrous oxide production from triplicate sets of composite soil microcosms brought to a soil gravimetric water content of 20% with water that did or did not contain ethanol (0.2%, ETOH). Error bars represent the standard error of the mean.

An objective of the pilot study is to reduce nitrate levels in the source area as efficiently as possible; to shorten the number of years that the source area planting needs to be irrigated. Results indicate that moisture and carbon content are consistently co-limiting factors for denitrification in the irrigated, source-area plantings. Denitrification could potentially be accelerated by increasing the volume of water added during the growing season, by irrigating on a 4 hour rather than 2 hour daily schedule, and by injecting ethanol into the lines to provide a supplemental carbon source.

3.2 Natural Attenuation of Ground Water

The pilot studies are evaluating natural attenuation as the primary remedy for ground water contamination at Monument Valley. Several natural processes may be acting to decrease nitrate and sulfate levels in the alluvial aquifer. The pilot studies are designed to acquire field data needed to estimate the capacity of natural attenuation processes. The goals for evaluating natural attenuation are to determine if the capacity of all natural processes acting to lower nitrate and sulfate levels in the alluvial aquifer both 1) exceed rates of contaminant loading from sources, and 2) will achieve remediation requirements in a reasonable time.

3.2.1 Plant Nitrate and Sulfate Uptake Rate

This task extrapolated nitrogen (N) and sulfur (S) contents of plant leaf samples determined for eight samples over the plume to estimate total S and N uptake the whole plume area, using the GIS data in Appendix A for plant cover estimates. Leaf material was harvested from 0.25 square meter (m^2) quadrats on eight randomly selected saltbush and greasewood plants growing over the plume. Dry weight of leaves plus seeds was multiplied by nitrogen content (3.14%, S.E. =0.29) or sulfur content (0.66%, S.E. = 0.04) then by fractional vegetation cover for areas of the plume to calculate annual nitrogen and sulfur uptake rates for the plume. (Saltbush nitrogen and sulfur values were used because greasewood results had not yet been returned by the laboratory by the time this report was written.) Both species replace their leaves annually hence the leaf weights were taken as a minimum measure of annual elemental uptake rates (excluding branch growth). Dry weight of saltbush leaves was 508 grams per square meter (g/ m^2) (S.E. = 55) while greasewood was 276 g/ m^2 (S.E. = 32). We used the mean value of 392 g/ m^2 assuming an equal proportion of plants over the plume.

The plume was divided into three areas based on plant density (see Appendix A). Plume Areas 1 and 2 were in the dense phreatophyte cover over the hotspot of the plume, whereas Plume Area 3 was the sparse area beyond the hotspot. The results (Table 3–10) show that about 450 kilograms (kg) of sulfur and 2,300 kg of nitrogen are in the standing crop of phreatophytes over the plume. Results from enclosure studies show that plant biomass and therefore uptake rates can be greatly enhanced by protecting plants from grazing.

Table 3–10. Sulfur and nitrogen uptake by phreatophytes growing over the plume, based on percent vegetation cover and elemental analyses (See Appendix A for map of area numbers and names.

Area No.	Area name	Total Area (m²)*	Plant Cover (%)	Dry-weight Leaves (kg)	Total S Uptake (kg)	S Uptake (area) g/m²	Total N Uptake (kg)	N Uptake (area) g/m ²
16	Plume 1	49,230	24.13	4,657	30.7	0.62	13.8	2.97
17	Plume 2	206,430	9.75	7,890	52.1	0.25	248	1.20
18	Plume 3	1,620,632	5.24	33,289	220	0.14	1045	0.64

3.2.2 Plume Denitrification: ¹⁵N Enrichment

A 2005 study provided evidence that plume nitrate is enriched in ¹⁵N with distance away from the source area, and hence could be used as a signature for biological denitrification in the plume. The task in 2006 was to quantify the rate of plume denitrification based on nitrous oxide production in the laboratory, and by determining the ¹⁵N enrichment factor as denitrification proceeds. The effect of ethanol in stimulating denitrification in samples from the aquifer was also tested.

Plume sediment samples were collected with a geoprobe in the phreatic zone three distances, 106, 530, and 1,000 m (near wells 606, 677, and 653, respectively), away from the source area, to assay the ¹⁵N enrichment rate. The ¹⁵N enrichment rate is an indication of how much the drop in nitrate levels, between the source and the leading edge of the plume, can be attributed to microbial denitrification. Five 100 g subsamples of each soil was weighed and slurried at 1:1 with a solution of 300 milligrams per liter (mg/L) KNO₃ and artificial ground water, and then

incubated at 6 $^{\circ}$ C in microcosms. The headspace of these microcosms were evacuated of O_2 with Ar and subjected to 10% acetylene. Periodic headspace and aqueous samples were taken to verify N_2O production.

Samples were frozen for $NO_3^{-15}N$ analysis at a later date (results were not available at the time of reporting). Additionally, four plume soil samples (well 653 at 32 ft, well 677 at 32 ft, well 606 at 33 ft, and 606 at 34 ft) previously tested and proven to have denitrifying activity at 6 °C (Figure 3–10) were used to determine nitrous oxide production rates and ^{15}N enrichment in the presence of ethanol as a carbon source at room temperature. Soil slurries were made by adding 6 ml of a 167 mg /L NO_3 ^{-N} (or 1 mg N) solution supplemented either with or without 7.5 mg C as ETOH to 10 g of soil as follows (10 replicates of each):

- a. Treatment 1 (653-32): Nitrate + ethanol solution
- **b.** Treatment 2 (677-32): Nitrate + ethanol solution
- c. Treatment 3 (606-33): Nitrate + ethanol solution
- **d.** Treatment 4 (606-34): Nitrate + ethanol solution
- e. Treatment 3 (606-33): Nitrate only.

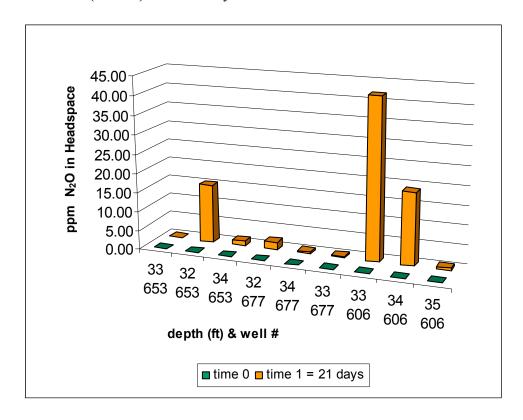


Figure 3–10. Nitrous oxide concentrations (ppm in moles) for headspace samples taken at time 0 and 21 days from replicate 1:1 soil slurries containing 30 mg of NO₃-N incubated at 6 °C.

A 10 ml sample of headspace gas was analyzed on a gas chromatograph for N_2O at the following time intervals: T_0 = 0 days, T_1 = 10 days, T_2 = 30 days, T_3 = 60 days and T_4 = 90 days. Also, at each sampling time point, two replicate samples were sacrificed and frozen to preserve the nitrate.

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Data presented in Figure 3–10 indicate measurable N_2O production after 21 days of incubation at 6 ^{o}C for samples taken at well 653 for the 32 ft depth, and at well 606 for both 33 ft and 34 ft depths. The measurable N_2O -N accounts for only a small fraction of the total N. The measured N_2O -N at 33 ft near well 606 accounts for 0.03% of the starting concentration. Hence, it will take some time to obtain samples that are measurably enriched in ^{15}N . In order to enhance this process, a second study was conducted whereby the soil slurries were supplemented with 7.5 mg of carbon and used only 1 mg of N.

Figure 3–11 shows high levels of nitrous oxide production for soil slurries containing ethanol compared to the sample without. To date roughly 60% of the initial N in nitrous oxide in slurries containing ethanol have been recovered. and will be submitting these sample for ¹⁵N analysis at the beginning of the year. These data also demonstrate that nitrate is naturally attenuated, albeit much more slowly than in the absence of ethanol.

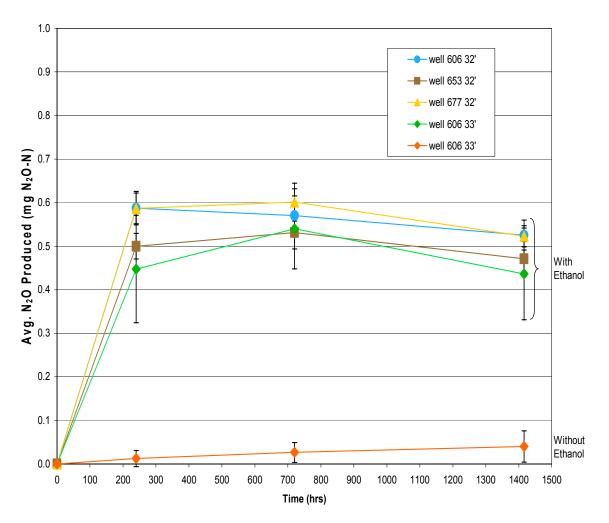


Figure 3–11. N_2 O-N production (mg) for headspace samples taken over 1400 h from replicate soil slurries supplemented either with or without C containing only 1 mg of NO₃-N and incubated at 23 $^{\circ}$ C.

These results confirm those obtained in 2005, showing that natural attenuation of nitrate—biological denitrification—occurs in the plume. The rates measured in laboratory microcosms are similar to rates calculated in 2005 from ¹⁵N enrichment measurements. The plume samples

without ethanol had rates of denitrification of about 3 micrograms N per kg of sediment per hour. A rough approximation of the time needed to remove half the nitrate in the plume at this rate is about 30 years, but this approximation contains simplifying assumptions about the volume of the plume and the distribution of denitrification activity within the plume. The assays showed considerable variability of denitrification rates among wells and at different soil depths. These assumptions can be tested with further sediment sampling. Rather than extracting sediment samples from the plume, it should be possible to assay denitrification in plume water samples. These samples could be drawn from existing monitoring wells over the plume.

In the presence of ethanol, the denitrification rate was 180 micrograms N per kg of soil per hour, 60 times faster than in sediment without ethanol. There is a great potential to clean up the nitrate in the hotspot area of the plume (Plume Areas 1 and 2 in Appendix A) through ethanol injection.

3.3 Enhanced Ground Water Attenuation

EA can be defined as initiating and/or augmenting natural and sustainable attenuation processes. The goal is to increase the magnitude of natural processes beyond that which occurs without intervention. EA approaches may be implemented if it cannot be shown with a high level of certainty that total capacity of *natural* attenuation processes are capable of attaining ground water remediation objectives. The pilot studies are focusing on enhancements that are sustainable—that do not require long-term, continuous intervention. The goals are to slow plume movement, extract nitrate and sulfate, and increase microbial denitrification.

3.3.1 Grazing Protection and Revegetation: Plant Growth and Nitrate and Sulfate Uptake

Preliminary studies found that protecting native *A. canescens* and *S. vermiculatus* plants from grazing can double biomass productivity, transpiration rates (water extraction from the aquifer) and nitrogen uptake rates. Preliminary studies also found that transplants could be successfully established, grow vigorously for several years in small exclosure plots, and with managed irrigation, send roots 30 ft into the nitrate and sulfate plume (DOE 2004c).

In 2005, two 50 m by 50 m plots within existing *A. canescens* and *S. vermiculatus* stands overlying the plume were fenced to protect plants from grazing (Grazing Exclosure Plots). The goal was to promote an increase in nitrate and plume water extraction. Fenced plots were constructed where the potential benefits of grazing protection were considered to be the greatest (DOE 2006). Grazing Exclosure Plot 1 contains a mature *S. vermiculatus* (black greasewood) stand to the north and a mixed stand of immature greasewood and *A. canescens* (fourwing saltbush) to the south. The plot was placed just east of a high nitrate area in the plume. Exclosure Plot 2 overlays a high nitrate area farther to the north. It contains a stand of fourwing saltbush ranging in maturity from new seedlings to mature, overgrazed plants. Two 50 m by 50 m fenced plots were also installed for a large-scale transplanting demonstration (Revegetation Plots). The two fenced plots are located in a denuded area overlying the proximal region of the plume with the highest nitrate concentrations. The plots also span a broad range of depths to ground water. Depths to ground water are about 30 ft for Revegetation Plot 1 and 40 ft for Revegetation Plot 2. Revegetation Plots were planted and irrigation began in spring 2006. Figure 3–12 show plot locations.

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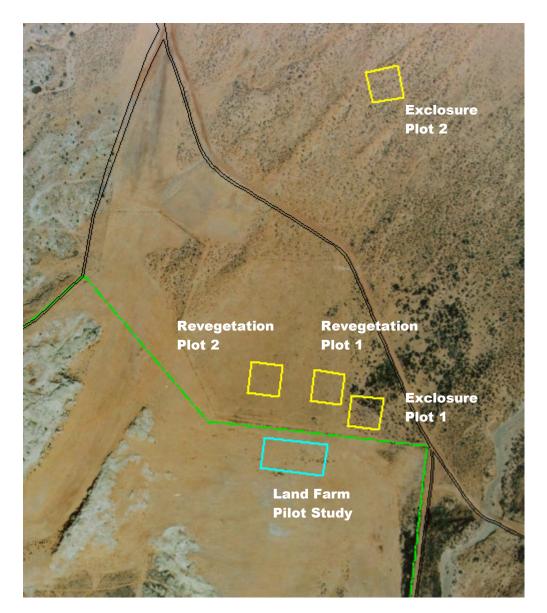


Figure 3–12. Aerial photograph (1997) of plume area showing GPS boundaries of grazing exclosures and revegetation plots (yellow), the land farm pilot study plot, and the millsite remediation fence line (green).

Leaf biomass and nitrogen and sulfur contents of eight mature saltbush and greasewood plants growing inside Grazing Exclosure Plot 1 were measured. The leaf and stem samples were collected in October, 2006, from 0.25 m² quadrats placed over plant canopies. Leaf biomass was 694 g/m² (S.E. = 145) for saltbush and 621g/m² (S.E. = 29) for greasewood. These values are significantly higher than values from plants not protected from grazing (Section 3.2.1). Results (Table 3–11) for saltbush and greasewood were averaged to estimate uptake rates since Grazing Exclosure Plot 1 contains an approximately even mix of the two plant types. Plant cover in plots were determined by analyzing the Quickbird image (Appendix A). Nitrogen (3.14%) and sulfur (0.66%) contents for saltbush leaves were used, as plant analyses for this task have not yet been returned by the outside laboratory. The Revegetation Plots 1 and 2 were in a formerly bare area. Biomass and nitrogen and sulfur uptake are still low.

Table 3–11. Estimates of annual nitrogen and sulfur uptake by plants in and out of enclosure plots. The sites are all located in the region designated as Plume Area 1 representing the hotspot of nitrate contamination.

Area #	Area name	Area (m²)*	Plant Cover (%)	Plant Cover (m²)	Nitrogen (kg)	Sulfur (kg)	Nitrogen (g/m²)	Sulfur (g/m²)
Area 11	Revegetation Plot 1	2,921	3.01	87.84	1.8	0.38	0.62	0.13
Area 12	Revegetation Plot 2	2,919	3.69	107.64	2.2	0.47	0.76	0.16
Area 13	Grazing Exclosure Plot 1	2,681	43.21	1,158.48	24.0	5.05	8.96	1.88
Area 14	Grazed area outside Exclosure Plot 1	2,687	19.15	514.44	10.7	2.2	3.98	0.82
Area 7	Natural regrowth inside DOE fence	12,087	68.75	8,310	172	36.2	14.2	2.99

Grazing Exclosure Plot 1 is in an that already had mature plants present. The plot was fenced in October, 2005, and an equal-sized control area around this plot was defined for comparison. By October, 2006, the Natural Exclosure Plot had over twice as much ground cover as the control area, and, therefore, projected nitrogen and sulfur uptake were also twice as high as in the control area.

Area 7 of Appendix A shows a longer term effect of grazing exclusion. This area now has 89% plant cover and high rates of nitrogen and sulfur uptake. This area was nearly devoid of vegetation in 1997 after the tailings pile was removed. Hence, grazing exclusion has had a major effect on vegetation density over the past 10 years. The enhanced vegetation cover contributes to passive remediation by controlling the movement of water downgradient, removing nitrogen and sulfur from the plume, and perhaps also by supplying carbon by its root system for denitrification in the phreatic zone above the plume.

3.3.2 Phreatophyte Transpiration Measurements

The plant community growing over the plume could potentially play an important attenuation role by controlling, through evapotranspiration (ET), the spread of the plume away from the site during the time it takes for natural denitrification to reduce nitrate to safe levels. Unfortunately, the plume area has been heavily grazed and plant cover is currently low. However, dense plant communities can develop when grazing is controlled (Section 3.3.1).

The purpose of this task was to estimate plant ET for the Grazing Exclosure Plot 1 and a Control Plot surrounding Grazing Exclosure Plot 1, and then to extend the findings to a greater area over the plume as a way to estimate how much ET could be enhanced by excluding grazing. Sapflow measurements were used to estimate ET for greasewood and saltbush plants growing in Grazing Exclosure Plot 1 and the surrounding Control Plot. Appendix B contains the full report with methods and analyses. The main findings are summarized below.

Analyses of satellite data from a Quickbird image (see Appendix A) indicated that plant cover inside Grazing Enclosure Plot 1 and the surrounding Control Plot were 43.21% and 19.15%, respectively. Mean daily transpiration rates inside and surrounding the plot were 4.45 millimeters per day (mm/day) and 1.98 mm/day in September 2006. These results show that restricting

grazing may enhance hydraulic control of the plume by more than doubling transpiration rates of native plants growing over the plume only a year of grazing control. A comparisons of plant cover in Grazing Exclosure Plot 1 in Area 7 (see Appendix A) suggests that plant cover and ET will continue to increase over time is grazing is managed.

Table 3–12 projects ET rates over three areas of the plume based on current and enhanced plant cover estimates (assuming grazing control produces a doubling of ET). Despite having the lowest plant cover, Area 18 (see Appendix A) has the greatest potential for enhanced ET due to its large area (450 ha). However, enhancing ET by controlling grazing in Areas 16 and 17 (71 ha) would have less impact on use of the range by residents and would likely help control water movement sown gradient. In this low rainfall region, enhancing vegetation cover and ET over the plume can potentially tip the water balance from recharge to discharge, accomplishing a major remediation goal—controlling the movement of the nitrate plume away from the site.

Table 3–12. ET projections for plume areas based on current percent cover and projected doubling of percent cover. September ET rates were projected to an annual rate based on a 210 day growing season and assuming mean ET was equal to half of peak ET over the growing season.

Plume Area	Area (m²)	Plant Cover (%)	Current Annual ET (m/yr)	Enhanced Annual ET (m/yr)	Current Total ET (m³)	Enhanced Total ET (m³)
Area 16	136,750	24.1	0.26	0.52	35,555	71,110
Area 17	573,416	9.8	0.11	0.22	61,070	122,139
Area 18	4,501,756	5.24	0.06	0.12	256,355	512,711

3.4 Active Ground Water Remediation: Land Farming

Land farming was selected as the most feasible and efficient *active* remedy for the nitrate and sulfate plumes. Land farming will be considered only if the more passive alternatives are found to be inadequate. The farm would serve several functions: (1) extract nitrates in irrigation water pumped from the plume; (2) convert nitrates into useful plant biomass; (3) reduce sulfate levels in the alluvial aquifer; (4) minimize water infiltration and leaching of contaminants back into the aquifer; and (5) enhance restoration of the disturbed ecosystem. Land farming consists of pumping the contaminated alluvial aquifer to irrigate and fertilize a farming operation on areas disturbed during the surface remediation. The land farm would produce a crop such as native plant seed for mine land reclamation. Pumping would continue until nitrate concentrations in the alluvial aquifer drop below the 44 mg/L maximum concentration limit for nitrate.

3.4.1 Soil Water Monitoring

The purpose of this task is to monitor soil moisture profiles, using a neutron thermalization hydroprobe, within land farm plots. Soil moisture monitoring is needed to detect seasonal wetting fronts and to manage irrigation rates. Hydroprobe ports installed in 1999 were used to monitor volumetric moisture content for each experimental treatment. Readings were taken at 0.3 m depth increments to the bottom of the ports (about 5 m). Soil moisture monitoring began prior to irrigation in March 2006 and continued through September 2006.

The treatment structure for the land farm pilot study consists of two main factors: (1) nitrate concentration in irrigation water supply and (2) two crops in the cropping system, *Atriplex* and *Sarcobatus*. There are four nitrate levels; no nitrate, 250 mg/L nitrate (a level not likely toxic to crop plants or to livestock feeding on the crop), 500 mg/L nitrate (a level not likely toxic to crops but possibly toxic to livestock), and 750 mg/L nitrate (a level possibly toxic to crops and livestock). Water is delivered to the landfarm via two wells: a clean water well pumped from the DeChelley aquifer and a well contaminated with nitrate (c.a. 750 mg/L nitrate), well 649. Plants in the control (or no nitrate) plots received 1 gallon of clean water per day. Plants in the 250 ppm nitrate plots were irrigated for 30 minutes with water from well 649 and 90 minutes with water from the DeChelley aquifer to total 1 gallon per day. Plants in the 500 mg/L nitrate plots were irrigated for 90 minutes with contaminated water and 30 minutes with clean water. Plants in the 750 ppm plots received 1 gallon of contaminated water per day from well 649.

In May 2006, it was noted that the pump at well 649 was drawing down and sucking air late in the 2 hour pumping cycle. The pump was installed just 0.6 m off bedrock and a shroud was placed over the well but this did not alleviate the problem. Hence, the higher nitrate treatment plots actually received less irrigation water than the others. This was reflected in the soil moisture measurements as presented in Figure 3–13; the overall soil profile is significantly (p < 0.05) drier for the 750 mg/L nitrate plot compared to the other treatments.

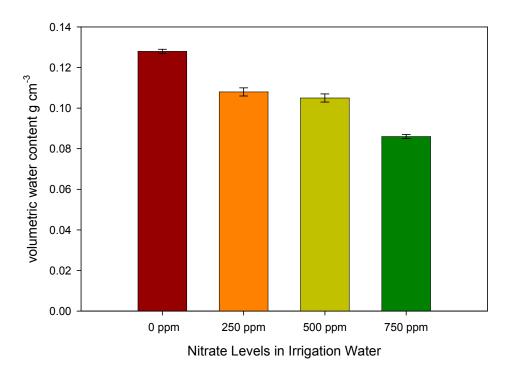


Figure 3–13. Average soil moisture across depth for each nitrate treatment level in the landfarm field. Soil moisture measurements were taken at 0.3 m intervals monthly in 16 ports randomly distributed through out the land farm.

One solution to poor production from well 649 might be to split the 2 hour irrigation cycle in to two 1 hour irrigations, one early in the day, one late in the day, allowing for recovery at

well 649. Another solution is to install an above ground storage tank adjacent to the well 649 with sufficient capacity to supply high nitrate irrigation requirement of 400 gallons per day to the land farm.

3.4.2 Crop Growth and Productivity

In October 2006, survival, growth, and productivity for the different combinations of crops and nitrate irrigation levels in the Land Farm were compared. Using the equation below and previous 2001 and 2005 subpile soil plant data (4,000 plants total), a sample size (*n*) of 60–140 plants was calculated as adequate to achieve plant canopy measurements with 10 percent accuracy and precision.

$$n = \frac{4\sigma^2}{\left(x * 0.1\right)^2}$$

where σ is the standard deviation of the established plants population mean and x is the population mean.

A total of 60 randomly distributed plants (3–5 plants per plot) were measured in the Land Farm. Shrub canopy area was estimated from cross-sectional diameters using the formula for an ellipsoid. Plant volume was estimated using the formula for a hemispheroid. Above ground biomass and total N were estimated based on a canopy volume-weight relationship established previously. Total N was determined for 16 individual plants sacrificed per plot by combustion on a CNS-2000 analyzer. Plant survival was estimated by census.

In June 2006, it was noted that many of the plants had been eaten down by rabbits despite efforts to replace them with new seedlings. Hervivory impactred *Sarcobatus* more than *Atriplex* as reflected in a high than average mortality rate (50%) measured for the Land Farm in the October 2006.

Nitrogen uptake was significantly (p < 0.05) greater for *Atriplex* plants harvested from the 750 mg/L nitrate plots compared to those receiving clean water (Figure 3–14a). However, estimates of total biomass (Figure 3–14b) were not significantly different between treatments. This was most likely due to variation in irrigation amount and not necessarily to nitrate toxicity effects. Additionally, plants receiving 750 mg/L nitrate took up as much total N as plants receiving 250 mg/L nitrate in the irrigation water reflecting the differences in plant growth.

Problems with irrigation volume and herbivory need to be addressed prior to the beginning of the 2007 irrigation season. Transplanting hardier, more mature, *Sarcobatus* and *Atriplex* plants in addition to enclosing the transplants in a biodegradable mesh cage may protect them from rodent damage.

3.4.3 Nitrification and Denitrification

Baseline soil nitrate and sulfate levels were determined in 2006 before the Land Farm was planted. Nitrate levels were variable over the field, ranging from below detection to >750 ppm. The levels are expected to change as irrigation with different treatment levels of nitrate begins.

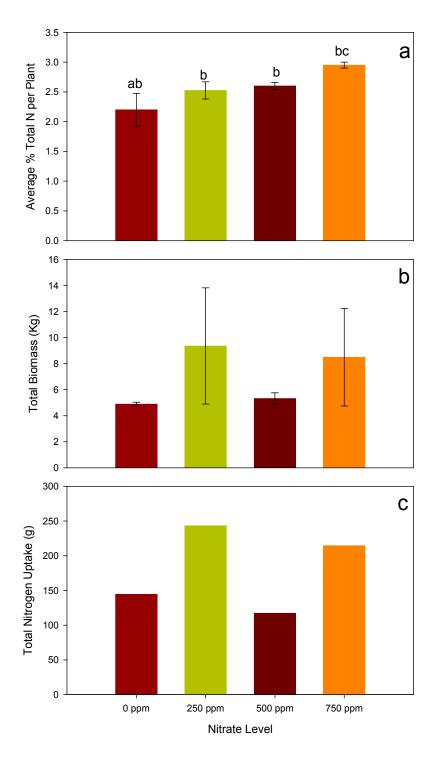


Figure 3–14. Average % N per plant (a), estimated total biomass (b) extrapolated from volume:biomass relationship times the number of live plants per plot, and the average amount of N (g) taken up by the plants (c). Error bars represent the standard error of the mean. Unlike letters indicate significant differences at alpha = 0.05.

Nitrate and denitrification rate were monitored once during the 2006 growing season. In August 2006, 16 soil cores were extracted and samples taken at 0.3, 1.2, and 2.4 m in accordance with the treatment structure for the study (Figure 3–15), for a total of 48 samples. The Land Farm is divided up into 16 plots with 4 replicates of 4 nitrate irrigation treatment levels, 0, 250, 500, and 750 ppm. The plots are further split into two different plant types: *Atriplex* and *Sarcobatus*.

Denitrification activity in the landfarm soil was assessed in soil microcosms containing a 10% acetylene headspace to prevent the conversion of N_2O to N_2 . Headspace samples were taken at 0, 24, 48, and 96 hours for N_2O analysis using a gas chromatograph equipped with an electron capture detector (GC-ECD). The rate of N_2O production in the headspace over time (ng N2O-N kg⁻¹ h⁻¹) is an indication of the denitrification activity of soil sample. Additionally, soil moisture, soil nitrate and soil ammonium were analyzed for each sample.

Average ammonium-N and nitrate-N levels are presented for each nitrate irrigation level in Figure 3–14 a and b. Average ammonium levels were significantly (p < 0.05) lower for the 500 ppm, but this trend was not consistent with depth. Soil nitrate levels were significantly (p < 0.001) higher for the 750 ppm nitrate irrigation level compared to the 0, 250 or 500 ppm nitrate levels at the 0.3 and 1.2 m depths but not the at the 2.4 m depth. Soil sampled from the 500 and 250 ppm plots appeared to have slightly higher nitrate concentrations than the 0 ppm plots, but the differences were not statistically significant.

Nitrous oxide production and gravimetric soil moisture are presented in Figure 3–14c. In general, N_2O -N production rates (ng N_2O -N kg dry soil⁻¹ h⁻¹) were very low with the maximum average rate of 0.05 in 750 ppm treatment plots at 2.4 m. There was a marginally significant linear correlation between moisture and nitrous oxide production (p < 0.1), yet no such relationship was observed with soil nitrate-N levels. Analysis of Variance using moisture as a covariant indicated a significant (p = 0.035) relationship between nitrous oxide production and moisture (Table 3–13). However, when nitrate and ammonium were analyzed in addition to soil moisture, this relationship was less significant (p = 0.061) suggesting that moisture explained only a small percentage of the variance in the nitrous oxide production measurements. Neither nitrate level nor depth had any influence on the amount of nitrous oxide produced.

Table 3–13. ANOVA for nitrous oxide production as the dependent variable with 3 depth levels and 4 nitrate irrigation levels. Moisture, nitrate-N and ammonium-N were analyzed as covariants. N = 48, Multiple R = 0.537, Squared Multiple R = 0.289

Source	Sum-of- Squares	df	Mean-Square	F-ratio	Р
Depth	0.797	2	0.399	1.076	0.353
Nitrate Irrigation Level	0.248	3	0.083	0.223	0.880
Depth & Nitrate Level	2.476	6	0.413	1.113	0.376
Moisture	1.391	1	1.391	3.752	0.061
Nitrate	0.406	1	0.406	1.094	0.303
Ammonium	0.001	1	0.001	0.002	0.962
Error	12.233	33	0.371		

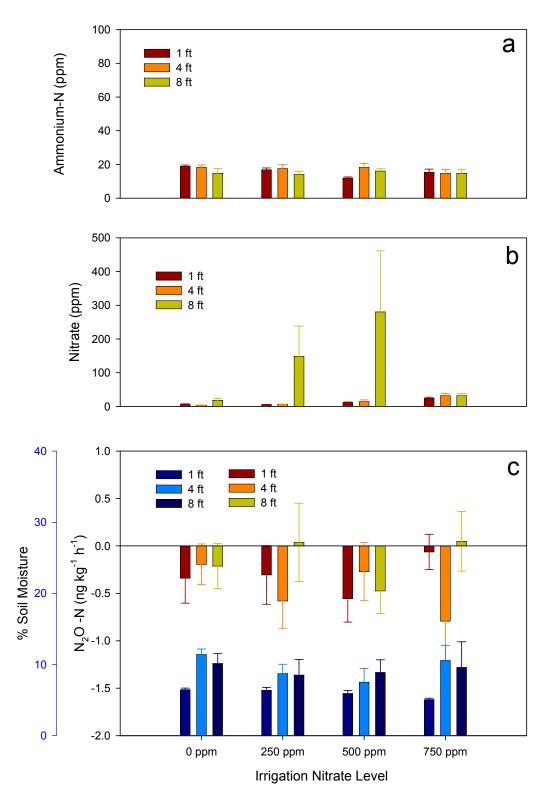


Figure 3–15. Average soil ammonium-N and nitrate-N levels are provided for each irrigation nitrate level (figures a and b, respectively). Nitrous oxide production and soil moisture content is present for each treatment in figure c.

4.0 Shiprock Pilot Studies

Shiprock was the site of a uranium-vanadium ore-processing mill that operated from 1954 to 1968. Mill tailings were contained in an engineered disposal cell in 1986. Ground water in the mill site area was contaminated by uranium, nitrate, and sulfate as a result of milling operations. The ground water system is divided hydrologically and physiographically into two regions, terrace and floodplain, that are separated by an escarpment. In March 2003, DOE began pump-and-treat remediation of ground water in the terrace area into an evaporation pond (DOE 2002). Ten extraction wells and two interceptor drains were expected to produce about 20 gallons per minute, but as of March 2004 they were producing only about half of that amount. In 2004, DOE reevaluated the site conceptual model for the Shiprock site and provided recommendations for improving the ground water treatment system (DOE 2004). One recommendation was to evaluate the feasibility of phytoremediation at the site, in this case the use of deep-rooted plants to enhance evapotranspiration of terrace water and thus limit the spread of contaminants.

Passive phytoremediation and hydraulic control is ongoing at Shiprock in the radon barrier borrow pit area and on the terrace between the disposal cell and the San Juan River floodplain. Volunteer tamarisk, black greasewood, and fourwing saltbush currently growing at the low end of the borrow pit area are extracting water, nitrate, and possibly other ground water constituents. A few scattered black greasewood plants that have established on the terrace above the floodplain are also removing small amounts of water that might otherwise daylight in seeps at the base of the escarpment. Higher rates of water extraction by woody plants in both locations would improve hydraulic control.

Planting these areas—enhanced phytoremediation—may be an economical addition to the current ground water compliance strategy. The success of enhanced phytoremediation would depend on several factors: depth to ground water, phytotoxicity of ground water constituents, site preparation methods, plant species selection, planting methods, soil amendments, and natural disturbances. The purpose of this pilot study is to begin evaluating the feasibility of phytoremediation at Shiprock.

4.1 Test Plot Locations, Design, and Installation

Test plot were set up in the borrow pit area and on the terrace between the disposal cell and an escarpment above the San Juan River floodplain (Figure 4–1). Plots are labeled by their location relative to each other: NE Escarpment; NW Escarpment; SE Borrow Pit; and SW Borrow Pit. Soil samples for the borrow pit area were analyzed and reported in 2005. Soil samples from new plots on the escarpment have been submitted for texture and chemical analyses at IAS Laboratories, Phoenix.

Two 50 ft by 50 ft hand-irrigated plots were designed for the escarpment. Each plot has small planting basins for 42 plants (7 plants each in 6 rows on 7 ft spacing). Plants are irrigated from a large elevated tank at each plot. A contractor on site keeps the tanks filled with water. Enough saltbush and greasewood plants were grown in the greenhouses at the University of Arizona to replant the two borrow pit plots and to plant the two new plots on the escarpment.

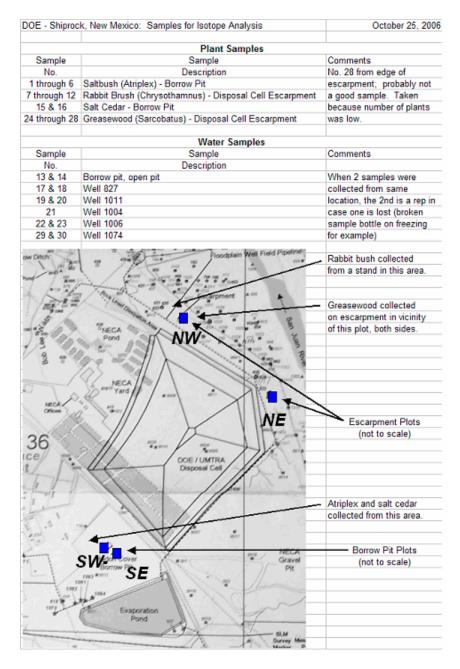


Figure 4–1. Location of test plots and locations of plants sampled for isotope analyses at Shiprock.

The soil in the escarpment plots was ripped with a bulldozer along planting lines. A 2 ft high rabbit fence was installed around plants and tanks were mounted on stands. Plots were planted in May, 2006. In the borrow pit plots, all dead plants were replaced with new saltbush or greasewood plants. In the escarpment plots, every third planting position was left unplanted to receive rabbitbrush when it is ready. The other planting positions were alternated between saltbush and greasewood plants (16 plants of each species). All plants were irrigated 3 times per week with 1 gallon of water per plant, May through October 2006.

4.2 Transpiration Water Sources

Oxygen and hydrogen isotope signatures were determined for plants growing naturally in the borrow pit and on the escarpment. Saltcedar and fourwing saltbush plants were sampled from the borrow pit area, and rabbitbrush and greasewood plants were sampled on the escarpment (Figure 4–1). Isotope analyses were performed by the SIRFER Laboratory at the University of Utah and are presented in Table 4–1. Results are summarized in Figure 4–2 and Figure 4–3.

Table 4–1. Isotope analyses of wells and stem samples.

SIRFER No.	Sample ID		DH	STDEV	¹⁸ O	STDEV
06-4048	1	Saltbush	-67	0.9	-6.6	0.3
06-4049	2	Saltbush	-62	0.3	-5.3	0.1
06-4050	3	Saltbush	-78	0.7	-7.4	0.2
06-4051	4	Saltbush	-67	0.2	-7.7	0.3
06-4052	5	Saltbush	-70	0.5	-7.7	0.1
06-4053	6	Saltbush	-67	0.7	-6.8	0.2
06-4054	7	Rabbitbrush	-64	1.0	-6.8	0.2
06-4055	8	Rabbitbrush	-70	1.1	-7.7	0.1
06-4056	9	Rabbitbrush	-72	1.1	-8.7	0.0
06-4057	10	Rabbitbrush	-73	0.8	-9.2	0.3
06-4058	11	Rabbitbrush	-75	0.6	-9.4	0.0
06-4059	12	Rabbitbrush	-71	1.8	-8.1	0.0
06-4060	13	Borrow Pit	-68	0.9	-7.4	0.3
06-4061	15	Salt Cedar	-70	0.4	-6.8	0.1
06-4062	16	Salt Cedar	-74	1.4	-7.6	0.1
06-4063	17	Well 827	-87	0.7	-10.0	0.0
06-4064	19	Well 1011	-89	0.0	-10.8	0.1
06-4065	21	Well 1004	-94	1.9	-11.0	0.1
06-4066	22	Well 1006	-77	0.5	-8.3	0.2
06-4067	24	Greasewood	-88	1.9	-7.9	0.0
06-4068	25	Greasewood	-85	1.1	-7.4	0.0
06-4069	26	Greasewood	-74	1.3	-7.2	
06-4070	27	Greasewood	-82	1.4	-8.3	
		,				
06-4071	29	Well 1074	-75	1.2	-7.2	

Isotope Signatures for Shiprock UMTRA Site Wells

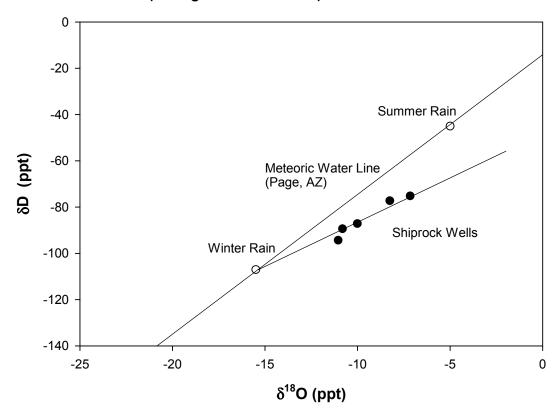


Figure 4–2. Plot of δ Deuterium vs. δ^{48} O in Shiprock well samples. Shiprock well samples appear to form an evaporation series originating from winter rain events. Data for meteoric water line and summer and winter rain are from Lin et al. (1996) for Page, Arizona.

Isotope Signatures in Shiprock Samples

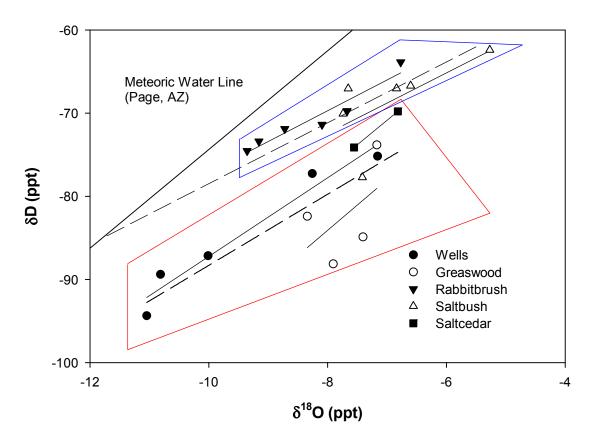


Figure 4–3. Plot of δ Deuterium vs. δ^{18} O in Shiprock stem-water and well samples. The meteoric water line, representing the line on which rain water falls, is shown as a solid line. The blue box encompasses saltbush and rabittbrush stem water samples, which appear to fall on a common line (dashed line). The red box encompasses well samples and greasewood and saltcedar samples, which appear to fall on a common line below the saltbush and rabbitbrush samples.

Figure 4–2 shows that the well samples fall along a common line plotting below the local meteoric water line (for Page, Arizona) (Lin et al. 1996). This indicates that the well samples form an evaporation series of water likely originating from a common source. As water evaporates it becomes more concentrated in heavy isotopes (¹⁸O and Deuterium) (less negative values relative to the seawater standard) compared to the original source. Based on Line et al. (1996), the well water is likely from winter rain events that partially evaporate as they infiltrate into the soil. Figure 4–3 plots the plant stem-water samples. Plant samples appear to fall into two clusters. Saltcedar and greasewood samples cluster along the evaporation line formed by the well samples, indicating that they are probably using ground water to support transpiration. On the other hand, saltbush and rabbitbrush form a separate evaporation series plotting above the well samples, and are probably using vadose zone water from rain events.

Saltcedar and greasewood, which are known to be phreatophytes, appear to be rooted into the ground water at the borrow pit and escarpment sites, respectively. On the other hand, rabbitbrush and saltbush appear to be using rainfall to support growth. Further samples from wells, soils, the containment cell (via the monitoring tubes), seeps below the cell on the flood plain of the San

Juan River, and summer and winter rain events should be analyzed to develop a more complete picture of the movement of water at the site, and its utilization by plants. Isotope analyses can be a powerful tool in tracking the sources of water and their environmental interactions at this site.

4.3 Monitoring

Plants were evaluated October 25. Escarpment plots had 100% survival. The SE and SW borrow pit plots had 86% and 79% survival, respectively. Ground squirrels are able to burrow under the fences in the borrow pit and remove plants. Table 4–2 gives the height and width of plants in each plot. Plants grew more in the escarpment plots than in the borrow pit plots, and saltbush plants grew more than greasewood plants in all plots. However, all plants grew substantially over the summer. Many of the saltbush plants produced seed.

Table 4–2. Size of plants in escarpment and borrow pit plots at the Shiprock UMTRA site, October 25, 2006. Values are means and standard errors of means.

Plot	Saltbush Height (cm)	Saltbush Width (cm)	Greasewood Height (cm)	Greasewood Width (cm)
NE Escarpment	60.4 (3.4)	59.4 (2.8)	42.2 (2.0)	38.5 (2.5)
NW Escarpment	56.4 (2.4)	55.8 (2.0)	40.6 (3.3)	42.9 (2.1)
SE Borrow Pit	49.6 (3.7)	33.6 (2.2)	29.2 (4.2)	21.5 (2.2)
SW Borrow Pit	41.6 (3.0)	23.7 (1.8)	24.3 (5.0)	16.1 (3.0)

5.0 References

- DOE (U.S. Department of Energy), 1996. Final Programmatic Environmental Impact Statement for the Uranium Mill Tailings Remedial Action Ground Water Project, DOE/EIS-0198, Grand Junction Projects Office, Grand Junction, Colorado.
- DOE (U.S. Department of Energy), 2002. *Phytoremediation of Nitrogen Contamination in Subpile Soils and in the Alluvial Aquifer at the Monument Valley, Arizona, Uranium Mill Tailings Site*, GJO-2002-312-TAR, U.S. Department of Energy, Grand Junction, Colorado.
- DOE (U.S. Department of Energy), 2004a. *Environmental Assessment of Ground Water Compliance at the Monument Valley, Arizona, Uranium Mill Tailings Site*, Draft, DOE/EA-1313, U.S. Department of Energy, Office of Legacy Management, Grand Junction, Colorado.
- DOE (U.S. Department of Energy), 2004b. *Phytoremediation of the Nitrogen-Contaminated Subpile Soil at the Former Uranium Mill Tailings Site in Monument Valley, Arizona: 2004 Status Report,* DOE-LM/GJ768-2004 (ESL-RPT-2004-07), Environmental Sciences Laboratory, U.S. Department of Energy, Grand Junction, Colorado.
- DOE (U.S. Department of Energy), 2004c. *Monument Valley Ground Water Remediation: Pilot Study Work Plan*, DOE-LM/GJ757-2004, Office of Legacy Management, U.S. Department of Energy, Grand Junction, Colorado.
- DOE (U.S. Department of Energy), 2006. *Soil and Ground Water Phytoremediation Pilot Studies at Monument Valley, Arizona: 2005 Status Report,* DOE-LM/1254-2006, Office of Legacy Management, U.S. Department of Energy, Grand Junction, Colorado.
- EPA (Environmental Protection Agency), 1999. *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites, Directive 9200.4-17P*, EPA Office of Solid Waste and Emergency Response, Washington, DC.
- Gee, G.W., A.L. Ward, T.G. Caldwell, and J.C. Ritter, 2002. "A Vadose Zone Water Fluxmeter With Divergence Control," *Water Resources Research* 38(8):35–41.
- Kim, K.C., and C.H. Benson, 2002. *Water Content Reflectometer Calibrations for Final Cover Soils*, Geo Engineering Report 02–12, Geo Engineering Program, University of Wisconsin-Madison, Madison, Wisconsin.
- Lin, G., S. Phillips, and J. Ehleringer, 1996. "Monsoonal precipitation responses of shrubs in a cold desert community on the Colorado Plateau," *Oecologia* 106:8–18.
- NRC (National Research Council), 2000. *Natural Attenuation for Ground Water Remediation*, National Academy Press, Washington DC.
- Savannah River National Laboratory, 2006. *Enhanced Attenuation: A Reference Guide on Approaches to Increase Natural Treatment Capacity*, WSRC-TR-2005-00198, Westinghouse Savannah River Company, Aiken, South Carolina, 160pp.

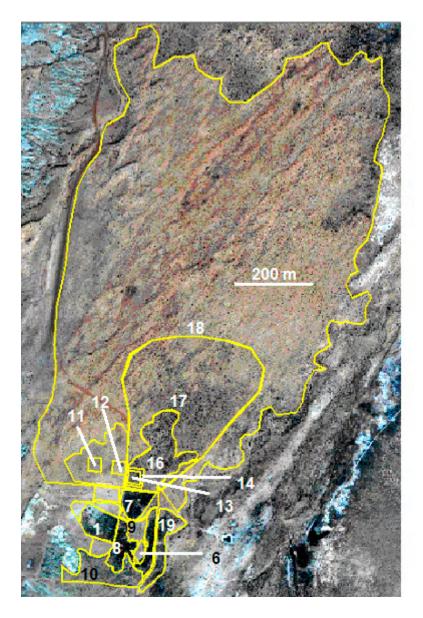
Savannah River National Laboratory, 2007. Advancing the Science of Natural and Enhanced Attenuation for Chlorinated Solvents, WSRC-STI-2006-00377, Final, Westinghouse Savannah River Company, Aiken, South Carolina.

Appendix A GIS of the Monument Valley UMTRA Site

Some of the tasks required an estimate of vegetation density of different areas of the site, in order to project sulfate, nitrate and water uptake by vegetation under different management scenarios. We acquired a Quickbird 60-centimeter (cm) resolution sharpened panchromatic image of the site in October 2006. We used an unsupervised classification program to determine the density of shrubs over the site. The classification program distributed each pixel into one of five classes based on spectral properties, using a cluster analysis procedure. When the classified image was compared to the original image, one class clearly corresponded to shrubs on the site. Shadows cast by the shrubs constituted another class, while soil, plant litter, and annual plants made up the other three mixed classes.

The accuracy of the classification procedure was tested by comparing cover estimates of areas that were determined by both ground measurements and Quickbird estimates. These areas were the four sections of the old planting in the subpile soil, and the newly planted sections of the subpile soil. The comparison showed a near 1:1 correspondence between the two types of estimates. The ground estimates were based on field measurements of a subsample of individual plants extrapolated to larger areas, hence, there is potential error in both methods of measurement.

The following images, tables, and photographs document the results of the GIS and present cover estimates for 19 sub-areas of the Monument Valley UMTRA site.



This overview image shows of areas documented in the following tables and sub-images.

Summary tables of all areas.

Estimated plant cover by QuickBird—Planted Areas

Area #	Area Name	Total Area (m²)ª	Pixels	Estimated Plant Cover (%)	Estimated Plant Cover (m ²)
Area 1a	4 Acre Field West	3729	3056	29.50	1100.16
Area 1b	4 Acre Field West Middle	4807	4884	36.58	1758.24
Area 1c	4 Acre Field East Middle	4541	7904	62.66	2845.44
Area 1d	4 Acre Field East	4255	8462	71.60	3046.32
Area 2	Extend field west	3016	24	0.29	8.64
Area 3	Extend field north	4374	128	1.05	46.08
Area 4	Extend field south	5427	441	2.93	158.76
Area 6	Evaporation pond	2859	785	9.89	282.60

^aby QuickBird

Estimated plant cover—Other Areas inside the fence

Area #	Area Name	Total Area (m²)ª	Pixels	Estimated Plant Cover (%)	Estimated Plant Cover (m²)
Area 7	Recruitment 1 (north)	12087	23084	68.75	8310.24
Area 7b	Sparse vegetated Area 1	3036	1622	19.23	583.92
Area 7c	Sparse vegetated 2	1049	212	7.28	76.32
Area 8	Recruitment 2 (west)	14372	24934	62.46	8976.24
Area 8b	Recruitment 3 (east)	10913	18831	62.12	6779.16
Area 9	Sparse vegetated Area 3	6501	818	4.53	294.48
Area 10	Recruitment 4 (south)	28071	21710	27.84	7815.60

^aby QuickBird

Estimated plant cover-Areas Outside the Fence

Area #	Area Name	Total Area (m²)ª	Pixels	Estimated Plant Cover (%)	Estimated Plant Cover (m ²)
Area 11	Enclosure west	2921	244	3.01	87.84
Area 12	Enclosure east	2919	299	3.69	107.64
Area 13	Enclosure natural	2681	3218	43.21	1158.48
Area 14	Control zone	2687	1429	19.15	514.44
Area 15	Sparse vegetated Area 4	43204	2196	1.83	790.56
Area 19	Recruitment 5	18212	23884	47.21	8598.24

^aby QuickBird

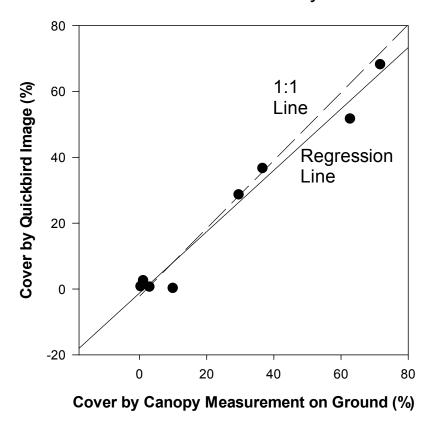
Estimated plant cover-Areas Over the Plume

Area #	Area Name	Total Area (m²)ª	Pixels	Estimated Plant Cover (%)	Estimated Plant Cover (m ²)
Area 16	Plume 1	49230	33002	24.13	11881
Area 17	Plume 2	206430	55885	9.75	20119
Area 18	Plume 3	1620632	235880	5.24	84917

^aby QuickBird

Area#	Area name	Area (m²)*	Plant Cover by Ground Measurement (%)	Plant Cover by Quickbird (%)
Area 1a	4 Acre Field West	3729	28.74	29.50
Area 1b	4 Acre Field West Middle	4807	36.74	36.58
Area 1c	4 Acre Field East Middle	4541	51.77	62.66
Area 1d	4 Acre Field East	4255	68.23	71.60
Area 2	Extend field west	3016	0.84	0.29
Area 3	Extend field north	4374	2.63	1.05
Area 4	Extend field south	5427	0.71	2.93
Area 6	Evaporation pond	2859	0.34	9.89
		* by QuickBird		

Ground Cover at Monument Valley UMTRA Locations



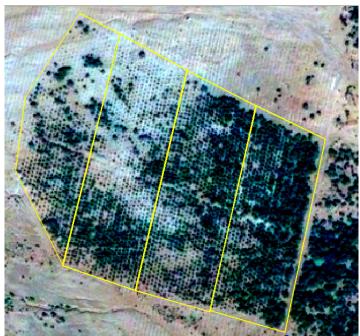
Regression of Quickbird GIS estimates of ground cover and estimates of ground cover by ground measurement of randomly selected canopy areas.

Individual Area Statistics

Existing area = Area 1 (a-d): 1999 4-acre Field (W, West Middle, East Middle, E), Extend fields N, W, S = Area 2 (EFW), 3 (EFN), 4 (EFS), Evaporation Pond = Area 6 (EP) All other Areas inside the fence = Area 7 to 10

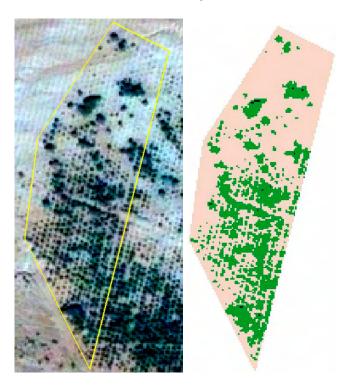
ERDAS/Digital Images

Area 1a-b 4 acre field part west, west middle, east middle and east



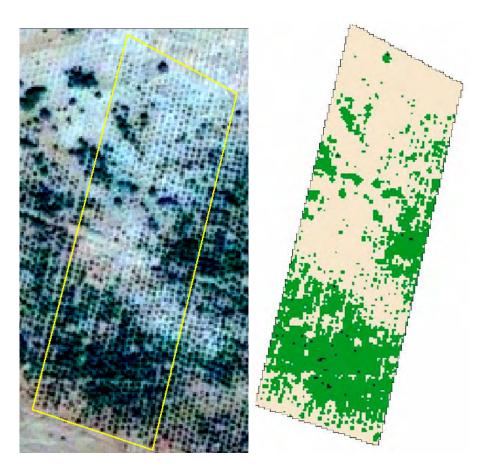


4 acre field part West Area 1a



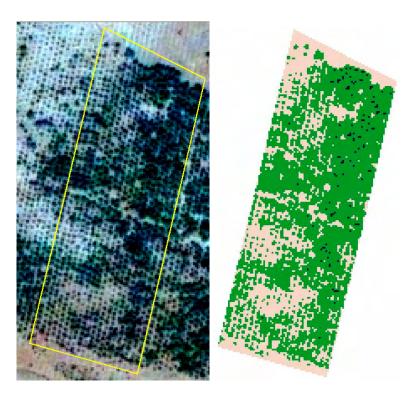
Area 1a	Pixels	Percent	Area (m²)
Shade	17	0.16%	6.12
Shrubs	3056	29.50%	1100.16
Other	7285	70.33%	2622.6
Total	10358		3728.88

Area 1b Established field West middle



Area 1b	Pixels	Percent	Area (m²)
Shade	34	0.25%	12.24
Shrubs	4884	36.58%	1758.24
Other	8434	63.17%	3036.24
Total	13352		4806.72

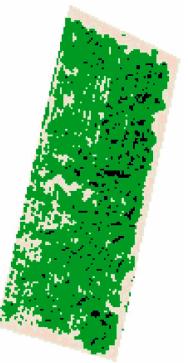
Established field East middle Area 1c



Area 1c	Pixels	Percent	Area (m²)
Shade	116	0.92%	41.76
Shrubs	7904	62.66%	2845.44
Other	4594	36.42%	1653.84
Total	12614		4541.04

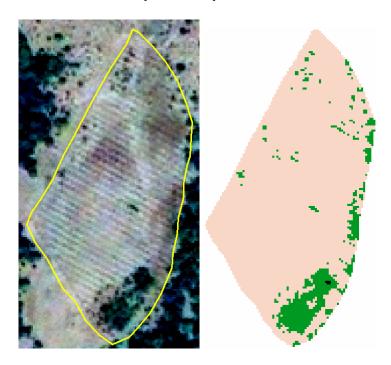
Area 1d Established field East





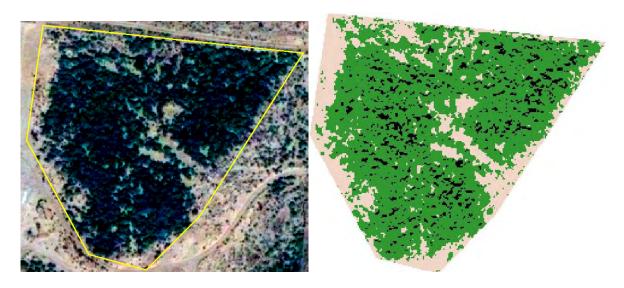
Area 1d	Pixels	Percent	Area (m²)
Shade	555	4.70%	199.8
Shrubs	8462	71.60%	3046.32
Other	2802	23.71%	1008.72
Total	11819		4254.84

Evaporation pond Area 6



Area 6	Pixels	Percent	Area (m²)
Shade	5	0.06%	1.8
Shrubs	785	9.89%	282.6
Other	7151	90.05%	2574.36
Total	7941		2858.76

Area 7a Recruitment 1 (North)



Area 7	Pixels	Percent	Area (m²)
Shade	2657	7.91%	956.52
Shrubs	23084	68.75%	8310.24
Other	7835	23.34%	2820.6
Total	33576		12087.36

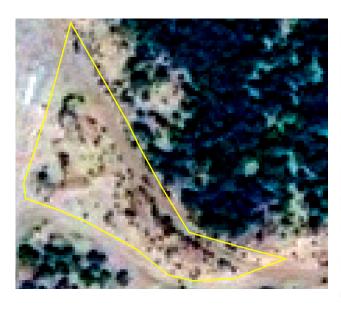
Area 7b Sparse vegetated Area 1

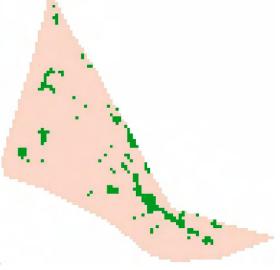




Area 7b	Pixels	Percent	Area (m²)
Shade	0	0.00%	0
Shrubs	1622	19.23%	583.92
Other	6812	80.77%	2452.32
Total	8434		3036.24

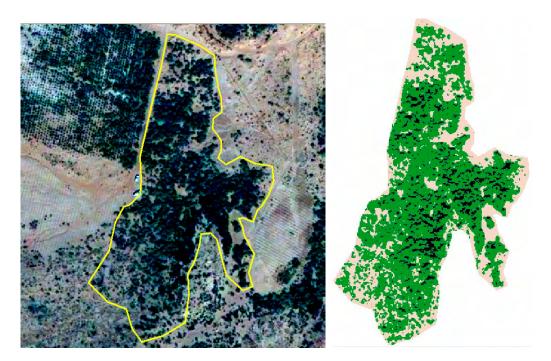
Area 7c **Sparse vegetated Area 2**





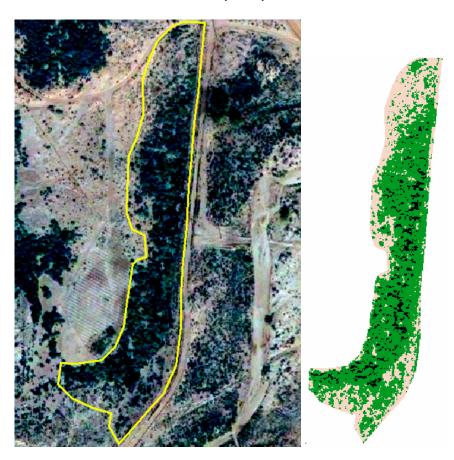
Area 7c	Pixels	Percent	Area (m²)
Shade	0	0.00%	0
Shrubs	212	7.28%	76.32
Other	2701	92.72%	972.36
Total	2913		1048.68

Area 8 Recruitment 3 (West)



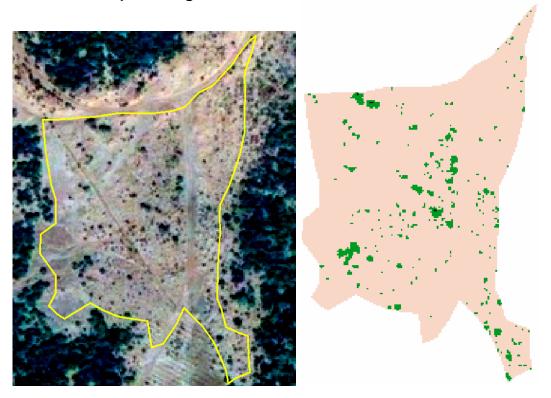
Area 8	Pixels	Percent	Area (m²)
Shade	3209	8.04%	1155.24
Shrubs	24934	62.46%	8976.24
Other	11778	29.50%	4240.08
Total	39921		14371.56

Recruitment 3 (East) Area 8b



Area 8b	Pixels	Percent	Area (m²)
Shade	2202	7.26%	792.72
Shrubs	18831	62.12%	6779.16
Other	9280	30.61%	3340.8
Total	30313		10912.68

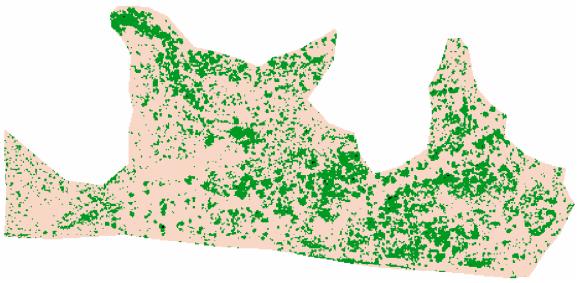
Area 9 Sparse vegetated Area 3



Area 9	Pixels	Percent	Area (m²)
Shade	5	0.03%	1.8
Shrubs	818	4.53%	294.48
Other	17235	95.44%	6204.6
Total	18058		6500.88

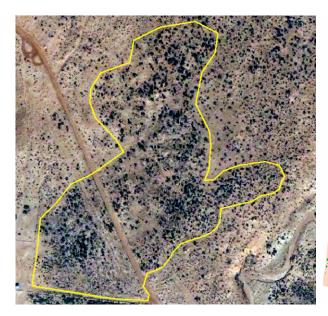
Area 10 **Recruitment 4 (South)**

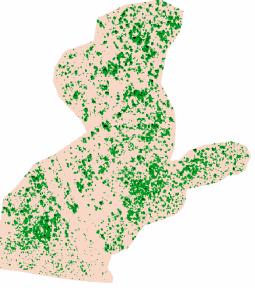




Area 10	Pixels	Percent	Area (m²)
Shade	55	0.07%	19.8
Shrubs	21710	27.84%	7815.6
Other	56211	72.09%	20235.96
Total	77976		28071.36

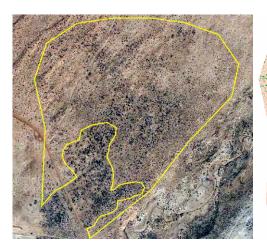
Area 16 Plume 1





Area 16	Pixels	Percent	Area (m²)
Shade	1107	0.81%	398.52
Shrubs	33002	24.13%	11880.72
Other	102641	75.06%	36950.76
Total	136750		49230

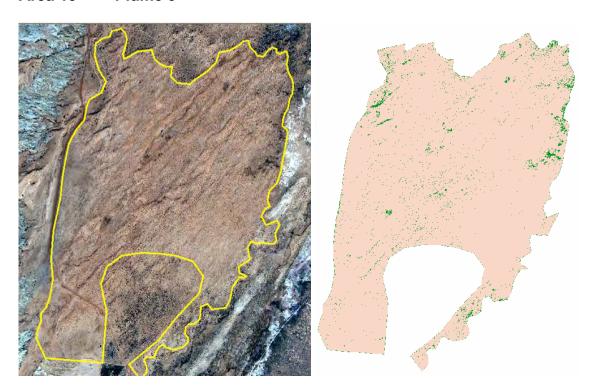
Area 17 Plume 2





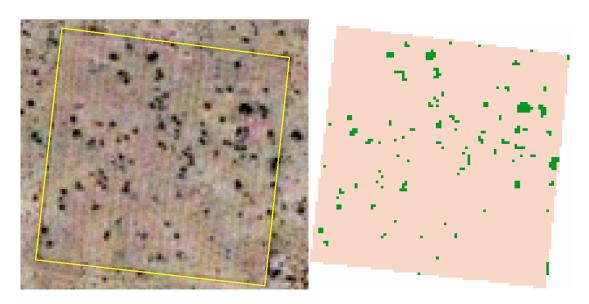
Area 17	Pixels	Percent	Area (m²)
Shade	708	0.12%	254.88
Shrubs	55885	9.75%	20118.6
Other	516823	90.13%	186056.3
Total	573416		206429.8

Plume 3 Area 18



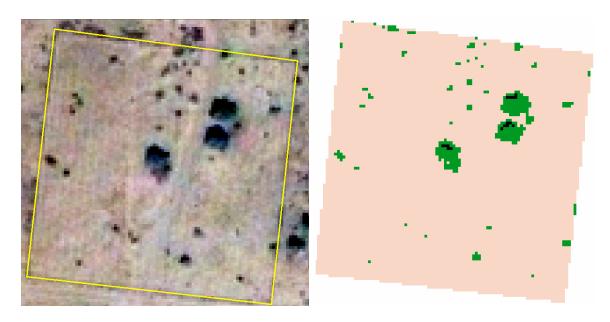
Area 18	Pixels	Percent	Area (m²)
Shade	592	0.01%	213.12
Shrubs	235880	5.24%	84916.8
Other	4265284	94.75%	1535502
Total	4501756		1620632

Area 11 Enclosure West



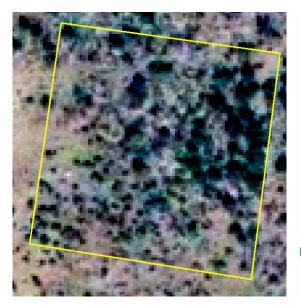
Area 11	rea 11 Pixels Percent		Area (m²)	
Shade	0	0.00%	0	
Shrubs	244	3.01%	87.84	
Other	7871	96.99%	2833.56	
Total	8115		2921.4	

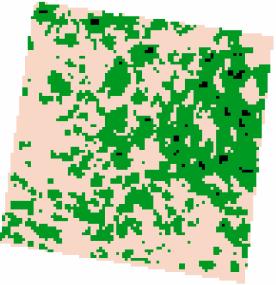
Area 12 **Enclosure East**



Area 12	Pixels	Percent	Area (m²)	
Shade	ade 16 0.20%		5.76	
Shrubs	Shrubs 299 3.69%		107.64	
Other	7792	96.11%	2805.12	
Total	8107		2918.52	

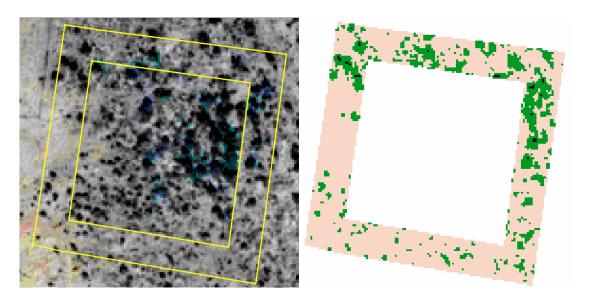
Area 13 Natural Enclosure (ET Site)





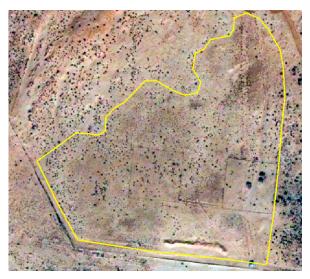
Area 13	rea 13 Pixels Percent		Area (m²)	
Shade	84	1.13%	30.24	
Shrubs	3218	43.21%	1158.48	
Other	4146	55.67%	1492.56	
Total	7448		2681.28	

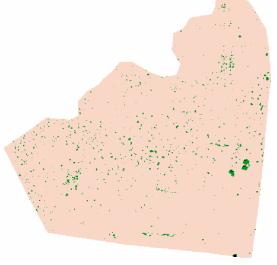
Area 14 Control Area (around Area 13)(ET Site)



Area 14	14 Pixels Percent		Area (m²)	
Shade	33	0.44%	11.88	
Shrubs	1429	19.15%	514.44	
Other	Other 6002 80.41%		2160.72	
Total	7464		2687.04	

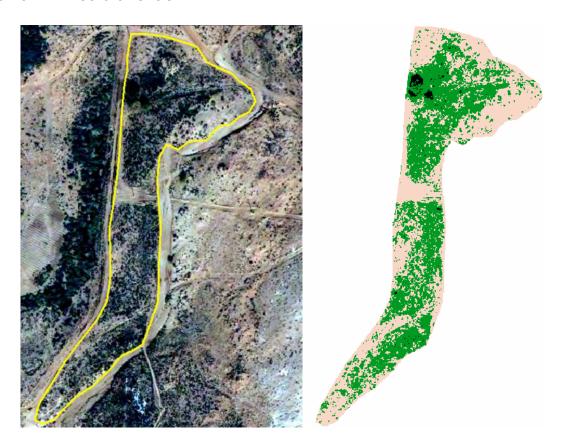
Area 15 **Sparse vegetated Area 4**





Area 15	Area 15 Pixels Percent		Area (m ²)	
Shade	31	0.03%	11.16	
Shrubs	2196	1.83%	790.56	
Other	117785	98.14%	42402.6	
Total	120012		43204.32	

Area 19 Recruitment 5



Area 19	Pixels	Percent	Area (m²)	
Shade	537	1.06%	193.32	
Shrubs	23884	3884 47.21% 859	8598.24	
Other	26168	51.73%	9420.48	
Total	50589		18212.04	

Photos were taken October 20th by Ulrike Kimmig during the fieldwork trip, at almost the same time the satellite picture was taken. The cars are at the same position on the satellite image. The photo gives a good impression of the differences in vegetation in the site.

Photo 1



Left background: 4 acre field (Area 1) Right background: recruitment area west (Area 8)

Foreground: extended field south (Area 4)

Facing: east north east

Photo 2



Right (background): 4 acre field (Area 1a-c) Left (Foreground): extended field south (Area 4)

Facing: westnorthwest

Photo 3

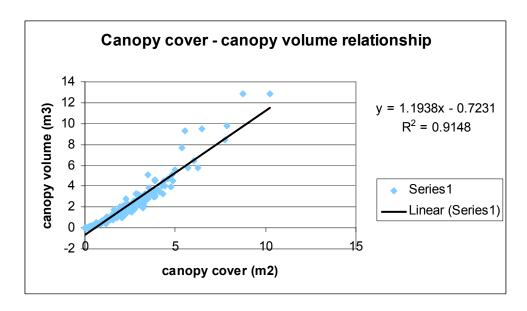


Sparse vegetated Area 1 (Area 7b) and 3 (Area 9) (Background: Comb Ridge) (facing: east)

Fieldwork data from the established field and the new plantings were used for the calculation of plant volume, dry-weight biomass, Nitrate and Sulfate uptake, which provided formulas acquired from the data

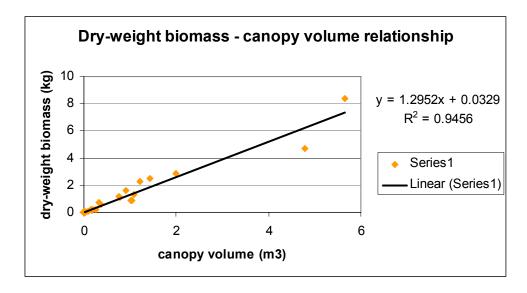
The plant **coverage (canopy)** was converted into plant volume, by using the formula acquired from the measured fieldwork data from the established field and the new plantings. Linear relationship between plant coverage in $m^2(x)$ and plant volume in $m^3(y)$: y=1.1938x-0.7231 as shown below:

Relationship between the canopy cover and the canopy volume (database: measurement of the 4 acre established field [Areas 1a-1d]).



The **dry-weight biomass** in kg (y) was calculated from the plant volume in m^3 (x) by using the linear relationship y=1.2952x+0.0329, as shown below:

Relationship between the canopy volume and the dry-weight biomass (database: current measurements of all proving grounds and data of former years).



Appendix B

Evapotranspiration Estimation Methods

The purpose of this task is to estimate plant ET for the Grazing Exclosure Plot and a Control Plot around the Exclosure Plot.

Methods

Sapflow

Sapflow was measured to estimate transpiration in greasewood ($Sarcobatus \ vermiculatus$) and saltbush ($Atriplex \ canescens$) plants using a heat balance approach (Sakuratani 1981, 1984; Baker and Van Bavel 1987). In this technique, a constant (and known) amount of heat is applied to a small diameter branch. Heat is subsequently dissipated either by convection or conduction. Convective losses involve the vertical transfer heat to the surrounding air, as well as heat transported by the sap; conductive losses involve lateral transfers of heat via the woody material of the branch. Using sapflow sensors designed following Kjelgaard et al (1997), we were able to directly measure vertical heat transfer (branch to air) and conductive losses via the wood. Convective losses of heat to sapflow (Q_f) were then computed as follows:

$$Q_{H} - (Q_{rad} + Q_{up} + Q_{dn}) = Q_{f}$$
 (1)

where Q_H is a known amount of heat applied to the branch; Q_{rad} is heat lost to the surrounding air; and, Q_{up} and Q_{dn} are measurements of heat lost to the wood by conduction above and below the heated branch segment. The heat balance component of sapflow (Q_f) is converted to mass flow (S) as follows:

$$S = 3600Q_f/4.19\delta T_{up-dn}$$
 (2)

where S is in g/hr; 4.19 is the specific heat of liquid water; 3600 is the number of seconds in an hour; and $\delta T_{up\text{-dn}}$ is the difference in temperature of the wood above and below the heated segment. Outputs from the gauges were recorded continuously by an automatic data logger.

Initially, a total of 37 sensors were deployed to measure sapflow on 31 plants. We affixed sensors to an approximately equal number of plants of each species inside and outside of the 50×50 m exclusion plot. Unfortunately, through the course of our data collection period, many of the sensor cables were rendered ineffective by rodents. Nevertheless, the final set of functional sensors provided a satisfactory representation of species and location (Table B–1).

Table B–1. The number of plants(branches) for each species and location—inside and outside the exclusion plot. Bold numbers indicate the number of plants(branches) with functional sensors at the end of the data collection period.

Location Species	Inside	Outside
Atriplex	8(10) 5(5)	7(9) 5(6)
Sarcobatus	8(8)	8(10)

Biometric Measurements

Biometric measurements were made on October 11, 2006, for each sensored plant regardless of the status of sensor functionality by the end of the measurement period. Plant height and canopy width and length were measured. Canopy area was calculated based on the area of an ellipse. Canopy volume was calculated by multiplying plant height times canopy area.

Leaf area per plant was determined by employing a dry weight to leaf area relationship. We determined this relationship by harvesting five leaves from each plant and pooling them by group: IA, *Atriplex* inside the exclusion plot; IS, *Sarcobatus* inside the exclusion plot; OA, *Atriplex* outside the exclusion plot; and OS, *Sarcobatus* outside the exclusion plot. Leaf area for each group of sampled leaves was measured using the point-intercept method. The same leaves were then dried and weighed, yielding a specific mass associated with a specific leaf area for each group.

Leaf area was computed in two ways. First, for each sensored plant, we collected leaves from a canopy volume with a cross-sectional area of $\frac{1}{4}$ m² (50 cm × 50 cm). We then weighed the dried leaves and multiplied by the appropriate area-mass scalar as defined by the plant's species and location. This value was then converted to Leaf Area Index (LAI), a dimensional index representing total leaf area from a canopy volume projected onto its corresponding canopy area. LAI is widely used to make biomass comparisons between different plants and/or vegetation types. The second way that we computed leaf area was by harvesting leaves from all branches housing a functional sensor. We dried the leaves and similarly computed total leaf area for each branch by multiplying by the appropriate area-mass scalar. Leaf area of the sensored branch enabled us to compute branch-specific sapflow fluxes.

Analysis

For the subset of functional sensors (see above), data were summarized over a period of 11 days (September 8, 2006 [DOY251]—September 18, 2006 [DOY261]). To compute daily sap flow, data were first screened for negative sap flow rates (Allen and Grime 1995). These were set to zero before average hourly sap flow was computed. For each day, daily sap flow was subsequently computed by multiplying average hourly sap flow by 24.

Following normalization, daily sap flow among plants was compared by species and location using two-way ANOVA. We employed three methods of normalization: two based on leaf area and one based on the cross-sectional area of the sensored branch (SF_{xs}). In the first case of normalization by leaf area, total leaf area per sensored branch (SF_{br}) was used. In the second case, sap flow was normalized by multiplying SF_{br} with LAI from its respective plant ($SF_{br} \times LAI = SF_{gr}$). This measure of sap flow represents the rate of sap flow from a canopy projected on 1 square meter of ground area. In conjunction with fractional vegetation cover derived from satellite images, SF_{gr} was used to scale sap flow at the plant scale to sap flow on a landscape scale.

Normalization data for individual sensors using the three methods described above are shown in Figures B-1, B-2, and B-3. In each case, one or more of the experimental groups (IA, IS, OA, and OS) contained sensors recording a mean transpiration value for the period of observation

significantly different from the group's grand mean. Nevertheless, all data were used in two-way analyses of variance.

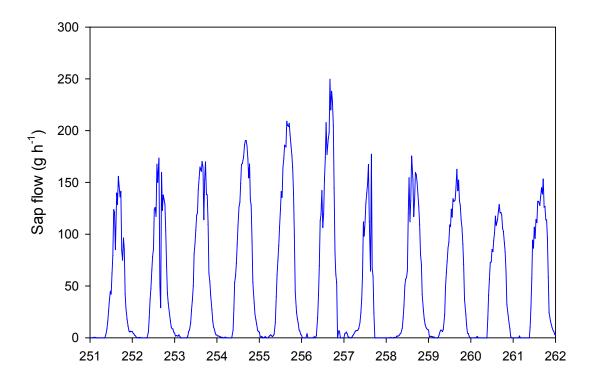


Figure B–1. Hourly sap flow for a single saltbush branch (IA10a) during the period of observation September 8th (DOY 251) to 18th (DOY 261).

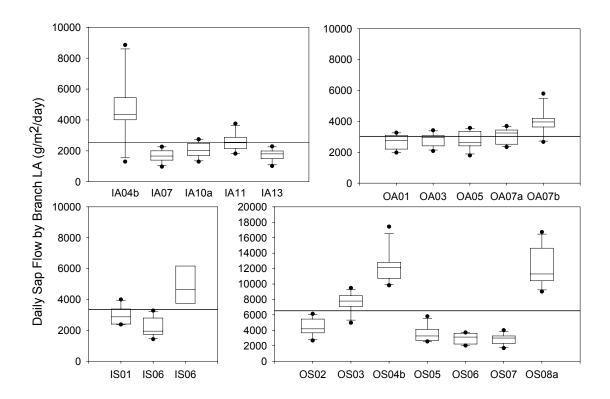


Figure B–2. Distribution of daily sap flow values normalized by branch leaf area. Horizontal lines show mean daily sap flow for each group. Note the different scale for Sarcobatus plants outside of the exclusion fence (Group OS).

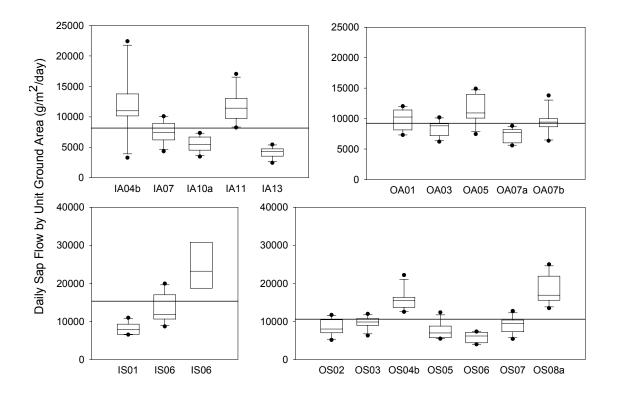


Figure B–3. Distribution of daily sap flow values normalized by leaf area projected on 1 m2 of ground area. Horizontal lines show mean daily sap flow for each group. Note the different scale for Sarcobatus plants inside and outside the exclusion fence (Groups IS & OS).

Results and Discussion

Biometric measurements

Our data indicate differences in plant canopy characteristics based on both species and location differences (Table B–2). In comparison to saltbush, greasewood had a larger stature and canopy volume both inside and outside of the exclusion plot. In both species, plants were larger inside the exclusion plot. The difference was especially pronounced in saltbush which had a canopy volume inside the plot that was roughly 8x the size of canopies outside the plot. Interestingly, however, LAI of saltbush inside and outside the exclusion plot was essentially equivalent.

These results show greasewood generally tend to be larger than saltbush plants but more importantly suggest that even after a single growing season, plant biomass is influenced by protection from grazing. In particular, the difference in canopy volume of saltbush inside and outside of the exclusion plots underscores livestock preference for this species. A two-way analysis of variance provided strong evidence that both species and location differences affect canopy volume (for both parameter estimates p<.0001); no effect was found for the interaction between species and location.

Table B-2. Biometric measurements (and associated standard errors) for all sensored plants.

	Height (m)	Canopy Volume (m³)	LAI
IA* n=8	1.09 (.061)	4.11 (1.32)	3.14 (.480)
IS n=8	1.71 (.091)	10.06 (1.74)	4.00 (.535)
OA n=7	0.70 (.073)	0.53 (.072)	3.04 (.345)
OS n=8	1.29 (.333)	3.90 (.338)	1.89 (.614)

^{*} IA = Atriplex plants inside exclusion plot; IS = Sarcobatus inside exclusion plot; OA = Atriplex plants outside exclusion plot; OS = Sarcobatus outside exclusion plot.

Analyses of LAI, however, reveal a somewhat different story. LAI was not influenced by species differences but was affected by location and the interaction between species and location (p<.013 and p<.024, respectively for two-way analysis of variance parameter estimates). The source for this outcome lies in the lower LAI found for OS compared to IS; similarly, its explanation is probably related to grazing. Both saltbush leaves and small branches are palatable to cattle. Indeed, much evidence of pruned saltbush plants was observed in the field. On the other hand, cattle generally avoid greasewood branches due their spines. Leaf area per plant is thus reduced with little corresponding impact on canopy dimensions, resulting in a decreased LAI.

Sapflow fluxes

Figure B–1 shows the typical pattern of daily sap flow variation. The diurnal fluctuation in sap flow rate is defined in amplitude by a maximum during the mid-afternoon and a minimum in the early morning before sunrise. Sap flow peaked progressively later over the course of the observation period, occurring at about 3:30 p.m. on DOY 251 and at about 5:00 p.m. on DOY 261. For this sensored branch, the average sap flow was 51.3 g/hr (minimum average = 40.5 g/hr on DOY 260 and maximum average = 71.1 g/hr on DOY 255).

For sap flow based on branch leaf area, averages range from 2,553.6 g/m²/day (Group IA) to 6,536.0 g/m²/day (Group OS). Among the four groups, OS stands out for its particularly high average sap flow (Figure B–2). This high value was largely influenced by two plants whose mean values exceeded the upper 95% confidence interval of the grand mean (upper 95% CI = 10,409.6 g/m²/day; n = 7). Despite this difference, there is no evidence to suggest that sap flow differs amongst the groups. Using a two-way analysis of variance it was determined that sap flow was not influenced by plant species, plant location or an interaction between the two (p = .0751, F-test).

For sap flow based on unit ground coverage, averages ranged from 8,144.0 g/m²/day (Group IA) to 15,291.4 g/m²/day (Group IS). In this case, the group average most different from the others is IS (Figure B-3). Amongst the four groups, IS has the lowest sample size (n=3); thus, its average value could be considered to be the least reliable. A two-way analysis of variance revealed that sapflow fluxes were not affected by differences in species, location or an interaction between species and location (p=.2035, F-test). The mean value across species and locations was

For sap flow based on branch cross-sectional area, averages ranged from 407.9 g/m²/day (Group OA) to 882.2 g/m²/day (Group IA). In contrast to sap flow data normalized by leaf area, there was strong evidence in these data that location was an important factor influencing

differences in sap flow rates (p-value for location in a two-way analysis of variance = .0025) where plants located outside of the exclusion plot tended to have lower sap flow rates (Figure B–4). These results closely track differences in the average total leaf area per branch in each of the groups. Group IA has the highest average total leaf area (0.49 m^2) per sensored branch while Groups OA and OS have similarly low values ($0.08 \text{ and } 0.09 \text{ m}^2$, respectively).

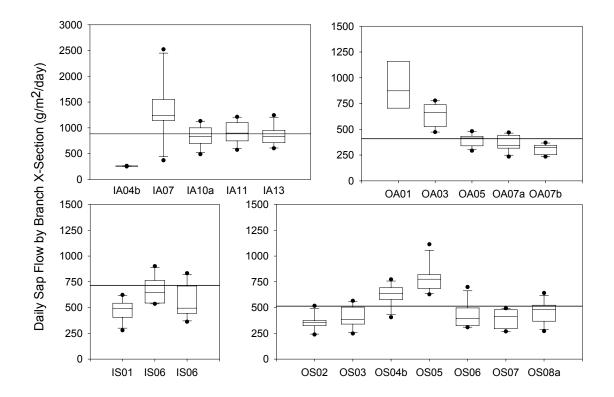


Figure B–4. Distribution of daily sap flow values normalized by branch cross-sectional area. Horizontal lines show mean daily sap flow for each group. Note the different scale for Atriplex plants inside the exclusion fence (Group IA).

Summary and Conclusions

We found strong evidence of differences in sap flow rates normalized by branch cross-sectional area where sap flow for similar-sized branches were lower outside compared to inside the exclusion plot. When normalized by leaf area, however, these differences were rendered insignificant. The absence of significant differences in the effect of species and location on sap flow normalized by leaf area means that these results can be pooled for scaling purposes. The grand mean of sap flow based on unit ground coverage (mean and 95% CI = 10346.6 ± 2222.2 g/m²/day) was therefore converted to mm/day of transpiration per m² of ground cover (mean and 95% CI = 10.35 ± 2.22 mm/day).

Analyses of satellite data from a Quickbird image (Appendix A), indicated that plant cover inside the exclusion plot was 43.21% and outside was 19.15%. Thus daily transpiration inside the plot was 4.45 mm/day and outside the plot was 1.98 mm/day. Transpiration rates outside the exclusion plot are comparable to evapotranspiration rates reported for a similar vegetation type at

a grazed site in southern Colorado (Cooper et al 2006). In that study, September values ranged from about 0.2 mm/day to about 2.8 mm/day. Transpiration rates inside the exclusion plot, however, are more similar to rates obtained during the peak transpiration months of July and August. Based on these results, we conclude that restricted grazing may enhance bioremediation efforts by enabling a potential twofold increase in transpiration rates of native plants at Monument Valley after only a year of grazing control. Plant density in Area 7 shows that plant density and therefore ET will continue to increase in subsequent years.

Recommendations: The ET measurments should be conducted over a full growing season and extended to include the newly planted exclosure plots. However, based on the results so far there appears to be a good potential to enhance passive remediation by enhancing vegetation cover and ET over parts of the plume. Table B–3 projects ET rates over three areas of the plume (Figure B–5) based on current vegetation density and enhanced density achieved by grazing control (assuming grazing control produces a doubling of ET). Despite having the lowest plant cover, Area 18 has the greatest potential for enhanced ET due to its large area (450 ha). However, enhancing ET by controlling grazing in Areas 16 and 17 (71 ha) would have less impact on use of the range by residents, and would control water movement away from the contamination hotspot. In this low rainfall region, enhancing vegetation density and ET over the plume can potentially tip the water balance from recharge to discharge, accomplishing a major remediation goal, which is controlling the movement of the contamination plume away from the site.

Table B–3. ET projections for plume areas based on current density and projected doubling of density. September ET rates were projected to an annual rate based on a 210 day growing season and assuming mean ET was equal to half of peak ET over the growing season.

Plume Area	Area (m²)	Plant Cover (%)	Current Annual ET (m/yr)	Enhanced Annual ET (m/yr)	Current Total ET (m³)	Enhanced Total ET (m³)
Area 16	136,750	24.1	0.26	0.52	35,555	71,110
Area 17	573,416	9.8	0.11	0.22	61,070	122,139
Area 18	4,501,756	5.24	0.06	0.12	256,355	512,711

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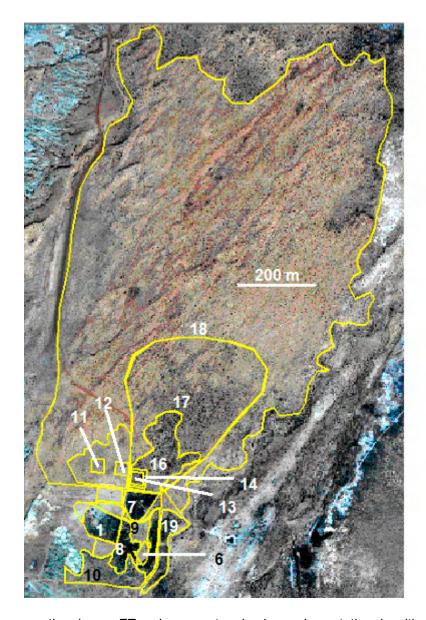


Figure B–5. Areas over the plume - ET under current and enhanced vegetation densities were calculated for Areas 16, 17, and 18 (Table 3.2.3).

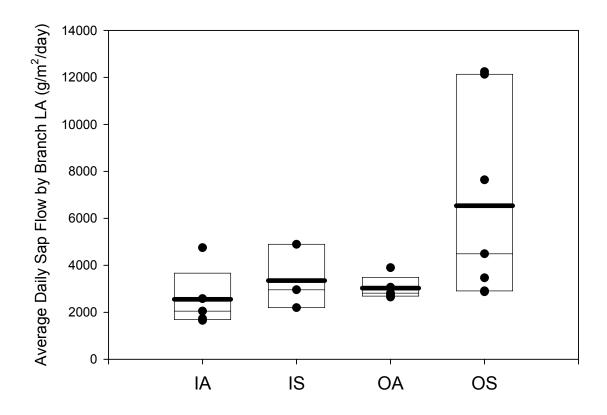


Figure B–6. Daily sap flow normalized by leaf area for sensored branches. Symbols represent daily sapflow flux averaged over the period of observation for each plant in each group. The thick line within the box is the group average; the thin line is the group median.

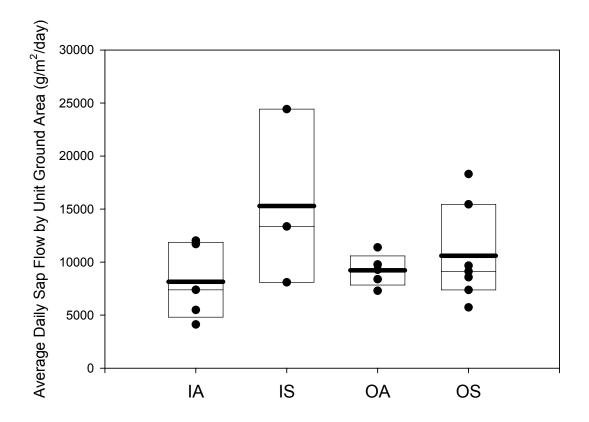


Figure B–7. Daily sap flow normalized by leaf area projected on 1 m² of ground area. Symbols represent daily sapflow flux averaged over the period of observation for each plant in each group. The thick line within the box is the group average; the thin line is the group median.

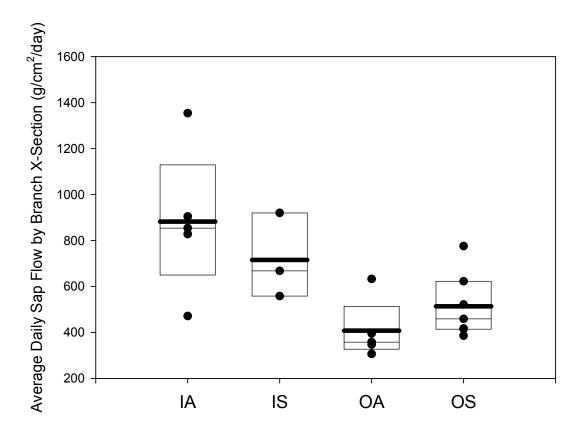


Figure B–8. Daily sap flow normalized by branch cross-sectional area. Symbols represent daily sapflow flux averaged over the period of observation for each plant in each group. The thick line within the box is the group average; the thin line is the group median.

Literature Cited

Allen, S.J., and V.L. Grime, 1995. "Measurements of transpiration from savannah shrubs using sap flow gauges," *Agricultural and Forest Meteorology*, 75:23-41.

Baker, J.M., and C.H.M. van Bavel, 1987. "Measurement of mass flow of water in the stems of herbaceous plants," *Plant Cell and Environment*, 10:777-782.

Cooper, D.J., J.S. Sanderson, D.I. Stannard, and D.P. Groeneveld, 2006. "Effects of long-term water table drawdown on evapotranspiration and vegetation in an arid region phreatophyte community," *Journal of Hydrology*, 325:21-45.

Kjelgaard, J.F., C.O. Stockle, R.A. Black, and G.S. Campbell, 1997. "Measuring sap flow with the heat balance approach using constant and variable heat inputs," *Agricultural and Forest Meteorology*, 85:239-250.

Sakuratani, T., 1981. "A heat balance method for measuring flux in the stem of intact plants," *Journal of Agricultural Meteorology*, 37:9-17.

Sakuratani, T., 1984. "Improvement of the probe for measuring water flow rate in intact plants with the stem heat balance method," *Journal of Agricultural Meteorology*, 40:273-277.

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established 1959

Task Order: ST07-100-02 Control No: 1000-T07-0897

May 9, 2007

Mr. Rich Bush Site Manager, LM-20 U.S. Department of Energy Office of Legacy Management 2597 B 3/4 Road Grand Junction, CO 81503

SUBJECT: Contract No. DE-AC01-02GJ79491, Stoller

Transmittal of the Natural and Enhanced Attenuation of Soil and Ground Water at Monument Valley, Arizona, and Shiprock, New Mexico 2006 Status Report.

Reference: FY 2007 Task Order No. ST07-100-02

Dear Mr. Bush:

Enclosed is a copy of the Natural and Enhanced Attenuation of Soil and Ground Water at Monument Valley, Arizona, and Shiprock, New Mexico, 2006 Status Report (April 2007). Also enclosed are four additional copies to be distributed to other recipients, including Navajo Nation UMTRA (2 copies), NRC (1 copy), and Navajo Nation EPA (1 copy),

This report presents 2006 growing season results of ongoing pilot studies to evaluate phytoremediation options for reducing nitrate and sulfate levels at Monument Valley, Arizona, and the use of plants to remove ground water at Shiprock, New Mexico. Because the Stakeholders and phytoremediation pilot study participants are the same for both the Monument Valley and Shiprock sites, the status of the 2006 studies have been combined into one document in an effort the make the reporting process more efficient.

If you have any question or comments, I can be reached on Extension 6652.

Sincerely,

David Miller Site Lead

(970) 248-6601

DM/lc Enclosures (5)

cc: File Project MON 400.02

cc wo/enclosures:

Clay Carpenter, Stoller (e) Jody Waugh, Stoller (e) File Project SHP 400.02